Lanthanoid complexes of a tripodal acetal ligand: synthesis, structural characterisation and reactivity with 3d metals

Stephen J. Archibald, Alexander J. Blake,*,† Simon Parsons, Martin Schröder*,†
and Richard E. P. Winpenny*

Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, UK

A novel tripodal ligand (H_3L^1) has been prepared by condensation of tris(2-aminoethyl)amine with 2,6-diformyl-4-methylphenol in MeOH. The compound has three equivalent side-arms, each containing four possible donor groups, an imine N atom, a phenol O atom and two O-donors from an acetal group. The crystal structure showed the arms to be arranged such that a non-crystallographic three-fold axis passes through the bridgehead N atom. Reaction of H_3L^1 with lanthanoid perchlorate salts resulted in the isolation of two series of complexes. With early lanthanoids compounds of stoichiometry $[Ln(H_3L^1)(H_2O)][ClO_4]_3$ were obtained and the compounds with Ln = La and Pr have been structurally characterised. The lanthanoid site in these complexes is ten co-ordinate, with a geometry which can be related to an icosahedron. For later lanthanoids, complexes of stoichiometry $[Ln(H_3L^1)][ClO_4]_3$ are found in which the lanthanoid site is nine-co-cordinate, with a tricapped trigonal-prismatic geometry. The complex with Ln = Y has been characterised by diffraction techniques. Mass spectroscopic studies indicated that the acetal functions within H_3L^1 are stabilised by co-ordination to the lanthanoid metals. Reaction of the complex $[La(H_3L^1)(H_2O)][ClO_4]_3$ with nickel(II) perchlorate led to a novel heterobimetallic complex in which both La and Ni are encapsulated within the tripodal ligand.

Compartmental ligands derived from Schiff-base condensation of 2,6-diformyl- and 2,6-diacetyl-4-methylphenol have received much attention.[1] These types of compound provide a framework from which polymetallic, and especially binuclear, metal complexes can be generated with considerable control of the topology and composition of the resulting complex.[1,2] In particular where heterobimetallic compounds are the desired product, design of a suitable polydentate ligand is a more elegant approach than use of simpler, less specific chelates. For example, Okawa and co-workers[3] have shown how ring expansion of one compartment of a Schiff-base macrocycle can allow complexation of both 3d and 6p elements by the same ligand. Recent work by Costes *et al.*[4] has shown that binuclear 3d/4f complexes can be made utilising such a route, whereas previous synthetic methods have always led to larger oligomers when such metals have been mixed.[5–9]

A second approach to the preparation of mixed-metal complexes is *via* the use of tripodal ligands where metals can be encapsulated by the three arms of a suitably designed ligand. In particular, Orvig and co-workers[10] have demonstrated that such ligands provide suitable hosts for lanthanoid metals, and the resulting complexes may be of use as contrast agents for magnetic resonance imaging (MRI). Related macrocyclic species have potential use in RNA and DNA cleavage,[11] and because of their photophysical properties.[12] McCleverty and co-workers[13] have also reported an interesting podand with chelating side-arms which appears ideal for co-ordinating to 4f elements.

We report herein the synthesis and structures of a free tripodal compartmental ligand and of its complexes with lanthanum, praseodymium and yttrium.[14] Additionally we demonstrate that its lanthanoid complexes can be deprotonated and a second metal incorporated within the tripodal host.

Experimental

Preparation of compounds

2,6-Diformyl-4-methylphenol was prepared by a literature procedure.[15] Tris(2-aminoethyl)amine (tren), lanthanoid salts and solvents were used as obtained. **CAUTION:** perchlorate salts are potentially explosive and should be handled with great care and in small quantities.

Proton NMR spectra in $CDCl_3$ (for H_3L^1) or CD_3NO_2 (for metal complexes) were recorded on a Bruker AM-360 MHz spectrometer referenced to $SiMe_4$, mass spectra by fast-atom bombardment (FAB) of samples in a 3-nitrobenzyl alcohol matrix on a Kratos MS50 spectrometer, and infrared spectra on a Perkin-Elmer Paragon 1000 FT-IR spectrometer as Nujol mulls. Analytical data were obtained on a Perkin-Elmer 2400 Elemental Analyser by the University of Edinburgh Microanalytical Service.

H_3L^1. 2,6-Diformyl-4-methylphenol (1.0 g, 6 mmol) was dissolved in MeOH (40 cm^3) and tren (2 mmol) dissolved in MeOH (10 cm^3) was added dropwise with stirring. The resulting yellow solution was stirred at 40 °C for 30 min then concentrated to 20 cm^3 under reduced pressure. Dimethyl sulfoxide (3 cm^3) was added with stirring and left to evaporate at room temperature. After 24 h brown-yellow crystals had formed which were filtered off and washed with Et_2O. Further crystals could be obtained by addition of MeOH and Me_2SO to the filtrate and continued evaporation at room temperature. Yield: 74% (Found: C, 65.5; H, 7.6; N, 7.7. Calc. for $C_{39}H_{54}N_4O_9$: C, 64.8; H, 7.5; N, 7.8%). IR (Nujol mull), cm^{-1}: 1636s, 1601s, 1273m, 1252m, 1104s, 1074s, 986m, 936m and 657w. ^1H NMR: δ 2.08 (s, 9 H), 2.81 (t, 9 H), 3.37 (s, 18 H), 3.47 (t, 6 H), 5.69 (s, 3 H), 5.89 (d, 3 H), 7.35 (d, 3 H), 7.76 (s, 3 H) and 14.2 (s, 3 H). FAB mass spectrum (significant peaks, possible assignments): *m/z* 691, $[H_3L^1 - OMe]^+$; 659, $[H_3L^1 - 2OMe]^+$; and 627, $[H_3L^1 - 3OMe]^+$.

$[La(H_3L^1)(H_2O)][ClO_4]_3$ 1. The compound H_3L^1 (0.14 g, 0.19 mmol) was dissolved in methanol (30 cm^3) at 40 °C and the solution filtered. Hydrated lanthanum perchlorate (0.11 g, 0.2 mmol) dissolved in MeOH (10 cm^3) was added dropwise; there was no immediate colour change but on stirring for 5 min a yellow precipitate was observed. The temperature was maintained and the solution stirred for 1 h. The yellow precipitate

---

† *Present address:* Department of Chemistry, The University of Nottingham, University Park, Nottingham, UK NG7 2RD.

was then filtered off and dried *in vacuo*. Yield: 84% (Found; C, 39.3; H, 5.2; N, 4.5. Calc. for $C_{39}H_{56}Cl_3LaN_4O_{22}\cdot CH_3OH$: C, 39.1; H, 5.1; N, 4.6%). FAB mass spectrum: *m/z* 879, $[La(H_3L^1)(H_2O)]^+$, 849, $[La(H_3L^1)(H_2O) - OMe]^+$ and 719, $[H_3L^1]^+$. A single crystal suitable for X-ray analysis was obtained by diffusion of diethyl ether vapour into a nitromethane solution of complex **1** at 258 K.

$[Pr(H_3L^1)(H_2O)][ClO_4]_3$ 2. This complex was synthesized in an identical manner to that described for **1** but with $Pr(ClO_4)_3\cdot xH_2O$ in place of lanthanum perchlorate. Yield: 80% (Found: C, 39.3; H, 5.4; N, 4.5. Calc. for $C_{39}H_{56}Cl_3N_4O_{22}Pr\cdot CH_3OH$: C, 39.0; H, 5.0; N, 4.6%). FAB mass spectrum: *m/z* 881, $[Pr(H_3L^1)(H_2O)]^+$; 851, $[Pr(H_3L^1)(H_2O) - OMe]^+$; and 719, $[H_3L^1]^+$. A single crystal suitable for X-ray analysis was obtained by diffusion of diethyl ether vapour into a nitromethane solution of **2** at 258 K.

$[Y(H_3L^1)][ClO_4]_3$ 3. This complex was synthesized in an identical manner to that described for **1**, but with $Y(ClO_4)_3\cdot xH_2O$ in place of lanthanum perchlorate. Yield: 79% (Found: C, 40.1; H, 5.6; N, 4.9. Calc. for $C_{39}H_{54}Cl_3N_4O_{21}Y\cdot CH_3OH$: C, 40.8; H, 5.3; N, 4.8%). FAB mass spectrum: *m/z* 810, $[Y(H_3L^1)]^+$. A single crystal suitable for X-ray analysis was obtained by diffusion of diethyl ether vapour into an acetonitrile solution of **3** at 258 K.

$[LaNiL^1(H_2O)][ClO_4]_2$ 4. Compound H_3L^1 (255 mg, 0.2 mmol) was dissolved in MeCN (20 cm^3) and hydrated nickel perchlorate (80 mg, 0.2 mmol) in MeCN (10 cm^3) was added dropwise causing a change to light green. Ethyldiisopropylamine (0.12 cm^3) was added with rapid stirring which was continued for 30 min. The solution was then concentrated to 5–10 cm^3. Slow addition of Et_2O gave a green solid which was filtered off. Yield: 6% (Found: C, 40.1; H, 4.6; N, 4.8. Calc. for $C_{39}H_{53}Cl_2LaN_4NiO_{18}$: C, 40.8; H, 4.7; N, 4.9%). FAB mass spectrum: *m/z* 1033, $[LaNiL^1(H_2O)(ClO_4)]^+$; and 1015, $[LaNiL^1(ClO_4)]^+$. A single crystal suitable for X-ray analysis was produced by diffusion of Et_2O vapour into an MeOH solution of complex **4** over a period of 3 d.

$[Gd(H_3L^2)(H_2O)_2][ClO_4]_{2.83}Cl_{0.17}$ 6. The complex $[Gd(H_3L^1)(H_2O)][ClO_4]_3$ **5** was synthesized in an identical manner to that described for **1**, but with $Gd(ClO_4)_3\cdot xH_2O$ in place of lanthanum perchlorate. It (150 mg, 0.12 mmol) was dissolved in MeCN (50 cm^3), then hydrated copper(II) perchlorate (44 mg, 0.12 mmol) in MeCN (10 cm^3) was added dropwise to give a light green solution. Ethyldiisopropylamine (3.2 cm^3 of a 0.1148 mol dm^{-3} solution in MeCN, 0.36 mmol) was added immediately and the solution stirred for 1 h at room temperature before being filtered and concentrated to half its original volume. Addition of diethyl ether produced a yellow-green precipitate in low yield which was filtered off. Yield: *ca.* 5% (Found: C, 35.1; H, 4.0; N, 5.4. Calc. for $C_{33}H_{40}Cl_3GdN_4O_{19.32}$: C, 37.2; H, 3.8; N, 5.3%). FAB mass spectrum: *m/z* 783, $[Gd(H_3L^2)(H_2O)_2]^+$; and 763, $[Gd(H_3L^2)(H_2O)]^+$. A single crystal suitable for X-ray analysis was produced by diffusion of Et_2O vapour into an MeCN solution of complex **6** over a period of 3 weeks.

Crystallography

Crystal data and data collection and refinement parameters for compounds H_3L^1, **1**–**4** and **6** are given in Table 1; selected bond lengths in Tables 2 and 3.

Data collection and processing. Data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device,[16] using graphite-monochromated Mo-Kα radiation (λ 0.710 73 Å) ω–2θ scans and on-line profile fitting.[17] Data were corrected for Lorentz polarisation effects. Semiempirical absorption corrections based on azimuthal measurements[18] were applied for all compounds.

Structure analysis and refinement. Structure H_3L^1 was solved by Patterson search techniques: a phenol fragment was located using the ORIENT and TRACOR routines of the DIRDIF suite.[19] All other structures were solved by direct methods using SHELXS 86[20] and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement. For H_3L^1 all non-H atoms were refined anisotropically with a similarity restraint applied to the three side-arms. In **1**–**4** the perchlorate anions and solvate molecules displayed considerable disorder which was modelled with partial site occupancies of several sites for oxygen atoms, and two orientations for the solvate molecules in **1** and **2**. For **1**–**3** all non-H atoms within cations and the Cl atoms of the anions were refined anisotropically. For **4** only metal atoms were refined anisotropically. For all structures H atoms were included in idealised positions, allowed to ride on their parent C atoms (C–H 1.08 Å), and assigned isotropic thermal parameters [$U(H) = 1.2U_{eq}(C)$ for aromatic H atoms; $U(H) = 1.5\ U_{eq}(C)$ for methyl H atoms]. Structures H_3L^1 and **1**–**4** were refined against F^2 using SHELXL 93.[21]

The crystal structure of complex **6** was refined by full-matrix least squares against *F* using CRYSTALS.[22] The long *c* axis and broad profiles of the diffraction peaks led to substantial peak overlap, while refinement was complicated by disorder in two of the three anion sites. One of these was modelled as a single perchlorate anion disordered over two orientations, while the other was modelled as being occupied by 0.83 ClO_4^-, disordered over two orientations, and 0.17 chloride, again disordered over two positions; the sum of the occupancies was restricted to unity. The perchlorate anions were treated initially as rigid groups and subsequently with similarity restraints on all Cl−O distances and O−Cl−O angles. Deviations in the angles in the minor components from 109° attests to the presence of further unresolved disorder. The geometries of the three equivalent side-arms of H_3L^2 were also restrained to be similar, and full-weight H atoms were placed in calculated positions and iteratively reidealised during refinement. Only the Gd and ordered ClO_4^- atoms were refined with anisotropic displacement parameters. Restrained anisotropic refinement of the ligand atoms, while possible, did not lead to any significant improvement, and so these atoms, together with atoms in the disordered anions and solvent molecules, were refined isotropically. The U_{iso} for the disordered O atoms in the anions was restrained to a common value. The two molecules of MeCN were made subject to explicit geometric restraints. The modelling of the electron density in the region of the mixed ClO_4^-/Cl^- site led to difficulties in full-matrix refinement, which diverged with symptoms associated with ill conditioning of the normal matrix. This was alleviated by the use of a combination of eigenvalue filtering and the application of shift-limiting restraints on the positional, thermal and occupancy factors of the part-occupancy Cl sites.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/302.

Results and Discussion

Synthesis and characterisation of H_3L^1

The compound H_3L^1 results from a reaction sequence which we had envisaged would produce the cryptand H_3L^3. Reaction of tren with 2,6-diformyl-4-methylphenol in MeOH leads to the expected Schiff-base condensation reaction of one formyl group with tren, but formation of a dimethyl acetal at the

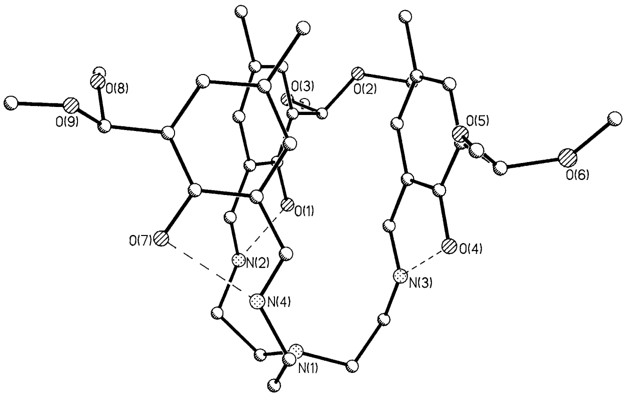


Fig. 1 Structure of H_3L^1 in the crystal showing the numbering scheme

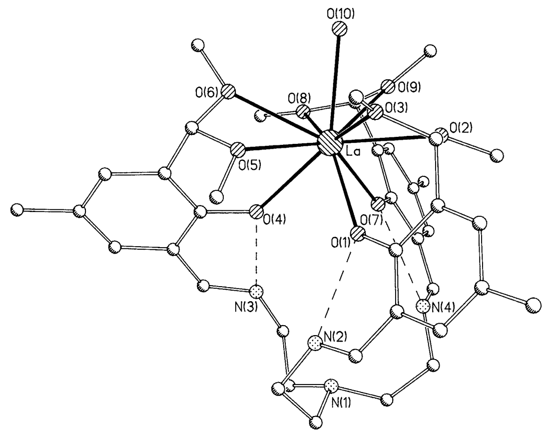
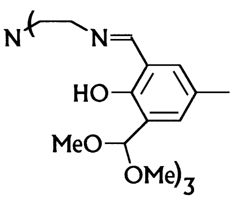
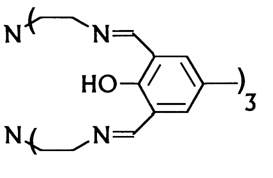


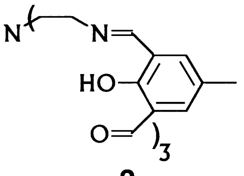
Fig. 2 Structure of complex **1** in the crystal showing the numbering scheme. The latter is common to **2**



H_3L^1



H_3L^3



H_3L^2

second group. It is worth noting that H_3L^1 is produced in very good yield, and that variation of the ratios of the reactants does not produce the cyclised H_3L^3 in this solvent, merely producing poorer yields of H_3L^1 and unreacted tren. The cryptand H_3L^3 has been made by Gagné and co-workers[23] by a two-step condensation of tren with 2,6-diformyl-4-methylphenol, and this synthetic strategy has been used by Nelson and co-workers[24] to produce related cryptands. The intermediate tripodal proligand isolated contained aldehyde functions, not acetals as in H_3L^1.

Spectroscopic characterisation of H_3L^1 does not decisively indicate its nature. The FAB mass spectrum does not show the molecular ion, only peaks at *m/z* 691, 659 and 627 due to loss of one, two and three methoxy groups respectively. Infrared spectroscopy confirms the disappearance of the carbonyl groups of the reactants, while NMR spectroscopy confirms a strong resonance due to the OMe groups of the acetal. Definitive proof of structure came from a crystallographic determination.

The compound crystallises with a non-crystallographic three-fold axis running through the bridgehead N atom (Fig. 1). This N atom is pyramidal and the lone pair is pointing towards the cavity formed by the arms of the compound. The orientation of the phenol rings within the three side-arms is such that the planes of these rings are at approximately 120° to each other and the potential donor groups within the arms, one N- and three O-donors in each, are pointing away from the central cavity. Although the H atoms were not located, all hydrogen bonding appears to be confined within each side-arm, with strong interactions likely between the imine N and the phenol O atom (average $N\cdots O$ 2.547 ± 0.020 Å): no significant interactions were found between molecules. Crystallisation of H_3L^1 could only be achieved by addition of Me_2SO to a MeOH solution yet no molecules of either solvent are found in the crystal lattice.

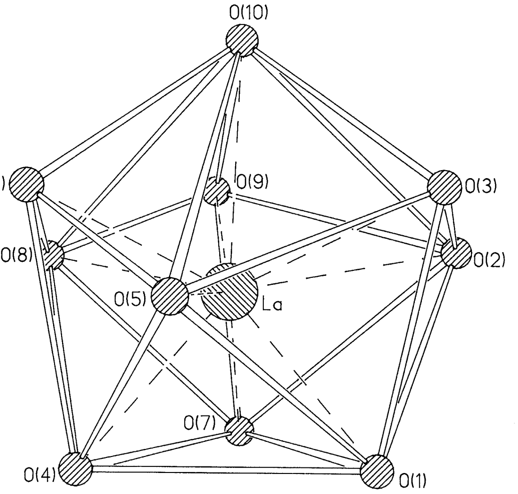


Fig. 3 The lanthanum co-ordination geometry in complex **1**

Synthesis and characterisation of lanthanoid complexes of H_3L^1

Reaction of a hydrated rare-earth-metal perchlorate salt with H_3L^1 in MeOH produces a yellow precipitate which analyses as $[Ln(H_3L^1)(H_2O)][ClO_4]_3$ for the larger, early lanthanoids, and as $[Ln(H_3L^1)][ClO_4]_3$ for the later lanthanoids. As representative examples of the early lanthanoids we have crystallised complexes where Ln = La and Pr (**1** and **2** respectively), and for the latter lanthanoids we have crystallised the yttrium complex **3**. Yttrium, although a 4d rather than a 4f element, forms compounds which are normally isostructural with those of the heavier rare earths.

Spectroscopic characterisation is again useful but not conclusive. The NMR spectra of **1** and **3** differ little from that of free H_3L^1, with a small shift to higher frequency observed for all resonances. Assignment of the various methyl resonances is complicated due to residual nitromethane in all samples. One intriguing change is that the resonance at δ 8.53, assigned to the CH proton of the imine function, appears as a doublet rather than as a singlet in the spectrum of H_3L^1 (δ 7.76). Irradiation of the resonance at δ 12.9 causes this splitting to collapse, indicating that the CH proton of the imine group is coupled to the proton involved in the hydrogen bond between the imine N and the phenol O atom of each side-arm. As this coupling is resolved for **1** and **3**, but not for H_3L^1, it seems likely that this H atom is more firmly located on the N atom in the complex, consistent with co-ordination of the phenol O atom to a metal centre. For **2** all resonances are broadened and shifted due to the paramagnetism of the Pr.

The FAB mass spectra of all three complexes show a peak for the molecular ion, and fragment peaks for loss of one MeO

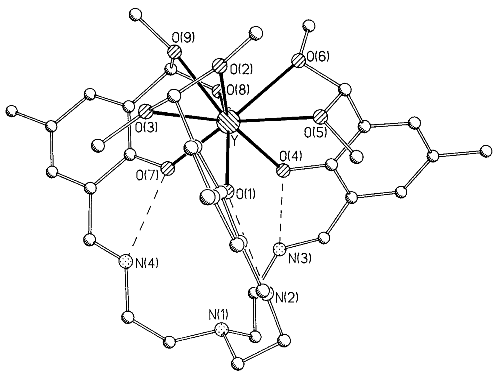


Fig. 4 Structure of complex **3** in the crystal showing the numbering scheme

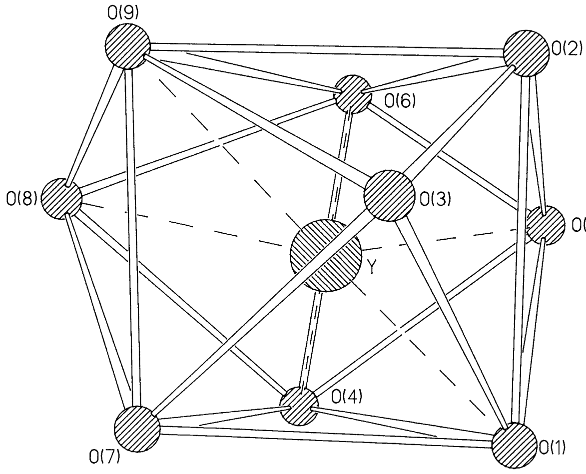


Fig. 5 The yttrium co-ordination geometry in complex **3**

group. By comparison with the spectrum of free H_3L^1, where the only peaks observed were for products where methoxy groups had been lost, these results suggest that co-ordination of the acetal side-arms to the metal has occurred thus stabilising the acetal functions.

Single-crystal X-ray diffraction studies show that compounds **1** and **2** are isostructural. In each the 4f metal is ten-co-ordinate, bound exclusively to oxygen donors. These are derived from all three side-arms, with two acetal and one phenolic oxygen attached from each leg of the tripod, and the final oxygen donated by a water molecule (Fig. 2). There is a non-crystallographic three-fold axis running through the metal site, the bridgehead N atom and the bound water molecule.

The Ln–O bond lengths depend on the type of oxygen atom, with bonds to phenol oxygens (for H_3L^1, average 2.47 Å) significantly shorter than bonds to acetal oxygens (for H_3L^1, average 2.65 Å) or to the water (for H_3L^1, 2.63 Å). There is also a predictable general shortening of these bonds moving from La to Pr due to the lanthanoid contraction. The co-ordination geometry around the Ln can be related to an icosahedron (Fig. 3) where the three phenolic oxygens [O(1), O(4) and O(7)] form a triangular face, the six acetal oxygens [O(2), O(3), O(5), O(6), O(8) and O(9)] form a puckered six-membered ring above this face and the final oxygen atom [O(10)] is at the centre of what would be the final triangular face. The geometry therefore corresponds closely to a trirhombohedron.

For complex **3** the co-ordination number of the metal has fallen to nine, with loss of the water molecule found in **1** and **2** (Fig. 4). Again the molecule has a non-crystallographic C_3 axis running through the metal and the bridgehead nitrogen. The Y–O distances show the same dependence on the character of the O atom, with shorter bonds to the O-donors from the phenol groups. The co-ordination geometry about the yttrium centre is now based on a tricapped trigonal prism (Fig. 5), and is comparatively regular. For example, the upper and lower triangular faces of the prism are essentially equilateral (angle range 59.0–61.7°), and the angles at the corners of the square faces are almost right angles (range 83.8–95.5°). It is interesting that the change in co-ordination number from ten in **1** and **2** to nine in **3** is achieved with retention of the three-fold axis through the metal centre.

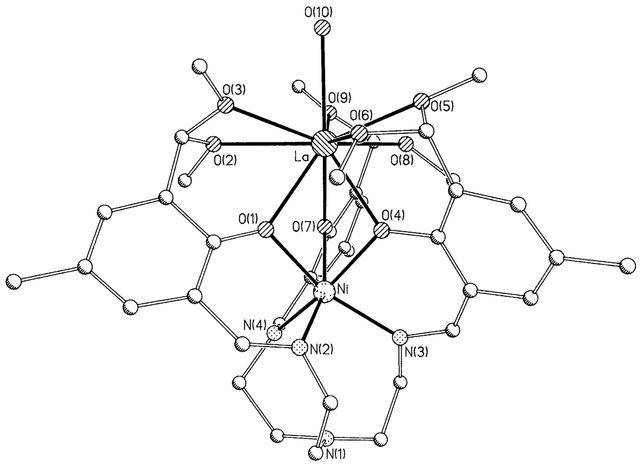


Fig. 6 Structure of complex **4** in the crystal showing the numbering scheme

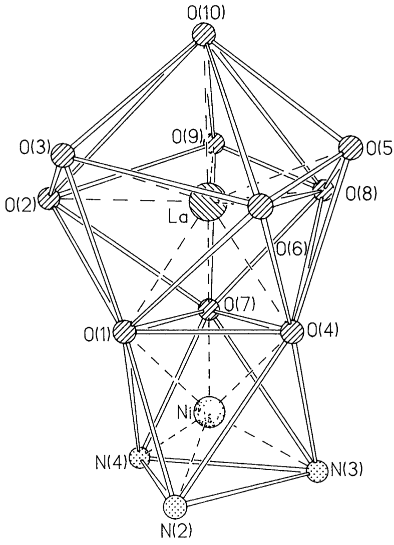


Fig. 7 The co-ordination geometries of La and Ni in complex **4**

No significant intermolecular hydrogen-bonding interactions are found in any of these structures, although strong intramolecular hydrogen-bonds between the imine N atom and the phenolic O atom in each side-arm are present. The second cavity of the compartmental ligand is therefore occupied by three protons in each of these complexes.

Co-ordination of metal ions to chelate acetal ligands is relatively rare. Binding of Rb[125] and Ag[126] to chelate acetal-containing antibiotics has been reported, while other non-chelate examples include binding of hard metal ions, usually main-group ions, to cyclic[27] and non-cyclic[28] acetals. However, no previous structural reports of lanthanide metal ions to acetals have been reported.

Reactions of lanthanoid complexes of H_3L^1

Given the structures of complexes **1**–**3** we argued that deprotonation of $[H_3L^1]$ to $[L^1]^{3-}$ would facilitate insertion of a second metal into the vacant octahedral cavity formed by the three imine N- and the three phenolic O-donors. This methodology proves moderately successful for a range of lanthanoids when

Table 1 Experimental data for the X-ray diffraction studies of compounds H_3L^1, **1**–**4** and **6**

	H_3L^1	**1**	**2**	**3**	**4**	**6**
Formula	$C_{39}H_{54}N_4O_9$	$C_{39}H_{56}Cl_3LaN_4O_{22}\cdot3CH_3NO_2$	$C_{39}H_{56}Cl_3N_4O_{22}Pr\cdot3CH_3NO_2$	$C_{39}H_{54}Cl_3N_4O_{21}Y\cdot3CH_3CN$	$C_{39}H_{53}Cl_2LaN_4NiO_{18}\cdot CH_3OH$	$C_{33}H_{39}GdN_4O_8\cdot2.83ClO_4\cdot0.17\ Cl\cdot2CH_3CN$
M	722.8	1361.3	1363.3	1233.3	1157.3	1152.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Trigonal	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$R3$	$P2_1/c$
a/Å	16.088(9)	13.013(3)	12.998(2)	17.381(13)	34.204(13)	10.845(10)
b/Å	13.353(10)	25.275(17)	25.265(8)	17.070(12)	a	11.641(11)
c/Å	18.798(23)	17.869(8)	17.771(3)	19.385(14)	24.59(3)	40.77(2)
β/°	93.92(5)	92.27(5)	92.282(12)	94.74		93.21(7)
U/Å^3	4029	5873	5831	5864	24914	5139
T/K	293	150.0(2)	150.0(2)	220.0(2)	150.0(3)	150.0(2)
Z	4	4	4	4	18	4
D_c/ g cm^{-3}	1.192	1.510	1.553	1.397	1.388	1.490
Crystal size/mm	0.1 × 0.1 × 0.1	0.2 × 0.2 × 0.2	0.70 × 0.43 × 0.27	0.4 × 0.4 × 0.1	0.55 × 0.15 × 0.08	0.61 × 0.33 × 0.15
μ/mm^{-1}	0.085	0.937	1.064	1.208	1.265	1.533
Unique data	6113	7604	10080	7628	4960	4883
Observed data	1810	5583	8917	4411	2032	2675
Parameters	477	719	760	632	300	576
Maximum Δ/σ ratio	−1.99	0.118	−0.75	−0.27	0.047	0.087 —
$R1$, $wR2^a$	0.0938, 0.3862	0.0500, 0.1439	0.0372, 0.1609	0.0553, 0.1830	0.1236, 0.5184	—
R, R'^b	—	—	—	—	—	0.1088, 0.1175
Weighting scheme,^{c} w^{-1}	$\sigma^2(F_o^2) + (0.1776P)^2$	$\sigma^2(F_o^2) + (0.0515P)^2 + 40.70P$	$\sigma^2(F_o^2) + (0.0418P) + 22.17P$	$\sigma^2(F_o^2) + (0.0835P)^2 + 20.71P$	$\sigma^2(F_o^2) + (0.013P)^2$	Chebychev three-term polynomial
Goodness of fit	1.068	1.034	1.040	0.987	1.201	1.100
Largest residuals/e Å^{-3}	0.54, −0.33	1.07, −0.76	0.75, −0.56	0.72, −0.54	2.00, −1.56	+1.94, −1.50

Common feature: all compounds crystallise as yellow tablets.

[a] SHELXL93:[21] $R1$ based on observed data, $wR2$ on all unique data. [b] CRYSTALS:[22] R and R' based on observed data. [c] $P = \frac{1}{3}[\max(F_o^2, 0) + 2R_c]$.

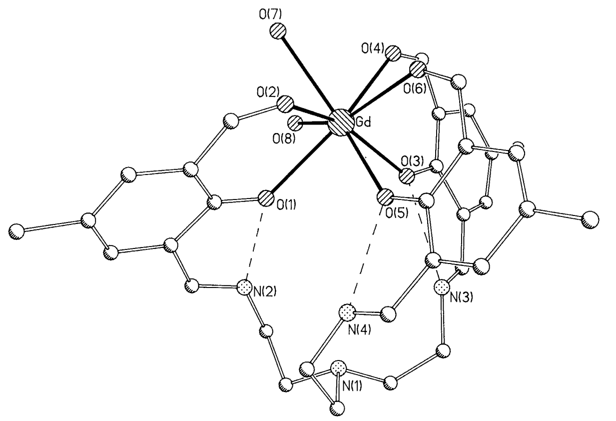


Fig. 8 Structure of complex **6** in the crystal showing the numbering scheme

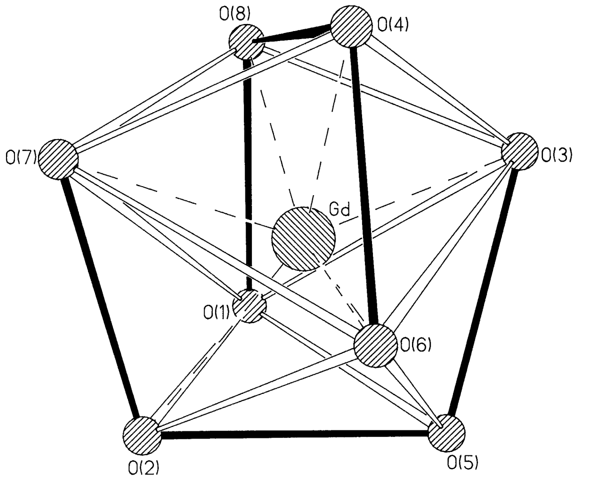


Fig. 9 The co-ordination geometry of Gd in complex **6**. The full lines show the O · · · O contacts within the mutually perpendicular trapezia of the dodecahedral oxygen array

Table 2 Selected bond lengths (Å) for compounds **1**–**3** and **6**

	1 Ln = La	**2** Pr	**3** Y	**6** Gd
Ln–O(1)	2.543(5)	2.396(3)	2.240(5)	2.31(1)
Ln–O(2)	2.650(5)	2.567(3)	2.432(5)	2.42(1)
Ln–O(3)	2.663(5)	2.613(3)	2.526(5)	2.31(1)
Ln–O(4)	2.462(5)	2.409(3)	2.230(5)	2.41(1)
Ln–O(5)	2.697(5)	2.658(3)	2.542(5)	2.32(1)
Ln–O(6)	2.631(5)	2.560(3)	2.400(5)	2.37(1)
Ln–O(7)	2.490(5)	2.438(3)	2.243(5)	2.40(2)
Ln–O(8)	2.587(5)	2.531(3)	2.526(5)	2.44(2)
Ln–O(9)	2.674(5)	2.654(3)	2.412(5)	
Ln–O(10)	2.626(5)	2.588(3)		

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

Ln–O(1)	2.44(2)	Ln–O(9)	2.62(2)
Ln–O(2)	2.72(3)	Ln–O(10)	2.60(3)
Ln–O(3)	2.57(2)	Ni–O(1)	2.07(2)
Ln–O(4)	2.45(2)	Ni–O(4)	2.07(2)
Ln–O(5)	2.58(2)	Ni–O(7)	2.05(2)
Ln–O(6)	2.67(2)	Ni–N(2)	2.07(3)
Ln–O(7)	2.43(2)	Ni–N(3)	2.08(3)
Ln–O(8)	2.64(2)	Ni–N(4)	2.09(3)
O(7)–Ni–N(2)	161.5(10)	O(1)–Ni–N(3)	160.9(10)
O(7)–Ni–O(1)	77.4(8)	O(4)–Ni–N(3)	84.3(11)
N(2)–Ni–O(1)	84.5(9)	O(7)–Ni–N(4)	84.3(10)
O(7)–Ni–O(4)	78.1(9)	N(2)–Ni–N(4)	96.3(10)
N(2)–Ni–O(4)	101.9(10)	O(1)–Ni–N(4)	103.4(10)
O(1)–Ni–O(4)	77.1(9)	O(4)–Ni–N(4)	161.8(10)
O(7)–Ni–N(3)	103.1(10)	N(2)–Ni–N(4)	95.6(11)
N(2)–Ni–N(3)	95.3(11)		

treated with nickel(II) salts, but markedly less successful with copper(II) salts.

Addition of 3 molar equivalents of dipropylamine to a 1 : 1 molar solution of complex **1** and $Ni(ClO_4)_2 \cdot 6H_2O$ in MeCN gives a green solution from which a green precipitate of a mixed La–Ni complex can be precipitated by addition of diethyl ether. Structural analysis reveals the binuclear complex $[LaNiL^1(H_2O)][ClO_4]_2$ **4** (Fig. 6). As expected the ligand $[L^1]^{3-}$ uses all twelve potential donor atoms to encapsulate a six-co-ordinate Ni^{II} and a ten-co-ordinate La^{III}. The trigonal axis, present in all the other structures involving H_3L^1, is also present in **4**.

The Ni^{II} is six-co-ordinate, bound to the three imine N-donors and three phenolic O-donors (Fig. 7). Significantly, the bond angles between the N atoms are markedly different from those of an ideal octahedron and all *trans*-N–Ni–O angles are reduced to *ca.* 161° by a trigonal compression imposed by the ligand. The strain within this cavity is perhaps most powerfully illustrated by considering the angles at the bridgehead sp^3-N atom [N(1)], which are close to 120°.

The three phenolic O atoms are shared with the La^{III}, which has a co-ordination geometry very similar to that in complex **1**. Therefore a face is shared by the 3d and 4f metals leading to a Ni · · · La contact of 3.355(5) Å. It is interesting that the geometry at La is closely maintained between **1** and **4**, with La–O bond lengths statistically unchanged (Fig. 7). It is the d-block metal ion which has a considerable distortion imposed on its geometry by the requirements of $[L^1]^{3-}$.

Similar products can be obtained for other 4f metals investigated (Ln = Gd^{III}, Er^{III} or Pr^{III}) when treated with $Ni(ClO_4)_2 \cdot 6H_2O$. The FAB mass spectra of the products always confirmed the formation of binuclear $[LnNiL^1][ClO_4]$ complexes, *e.g.* for **4** at *m/z* 1015. Elemental analytical data were less reassuring, and in most cases indicated the presence of some impurity beyond additional solvate molecules. This is reflected in low values for C, H and N. This suggests that encapsulation of two metals by H_3L^1 is difficult, presumably due to the trigonal strain imposed at the 3d-metal site.

The problems associated with addition of nickel to lanthanoid complexes of H_3L^1 become much more serious when copper(II) salts are utilised. The second trigonally compressed octahedral cavity is clearly incompatible with the requirements of the d^9 metal ion. All reactions produced compounds which do not contain both metals, and there is no indication from mass spectrometry that heterobimetallic complexes are formed. For example, reaction of $[Gd(H_3L^1)(H_2O)][ClO_4]_3$ **5** with $Cu(ClO_4)_2$ appears promising, but crystallisation gives crystals of a mononuclear gadolinium complex **6**. These crystals diffracted poorly, however the structure demonstrates that incorporation of a second metal has failed and that the ligand has been modified, with the acetal groups hydrolysed (Fig. 8), which reduces the number of available oxygen-donor atoms to six; three phenolic oxygens and three O-donors from aldehydes. Therefore in order to reach a satisfactory co-ordination number at gadolinium two water molecules are also present.

The Gd–O distances show a similar variation to that found for complexes **1**–**3**; bonds to phenolic O atoms are shorter (*ca.* 2.32 Å) than those to other O-donors (2.37–2.44 Å). The geometry of the eight-co-ordinated Gd can be related to a dodecahedron (Fig. 9), with the two intersecting mutually perpendicular trapezia required by this geometry described by O(1), O(8), O(4), O(6) and O(7), O(2), O(5) and O(3). It is also noticeable that the three-fold symmetry evident in the structures featuring H_3L^1 has disappeared, which suggests it is the steric requirements of the six OMe groups of the acetal functions which were causing the trigonal arrangement of the ligand.

Conclusion

Although the reaction to give H_3L^1 and related Ln–Ni complexes works, the strain at the bridgehead N atom in $[L^1]^{3-}$ incorporating ethylene linkages leads to some loss of the 3d metal from the inner co-ordination site during recrystallisation. This is further exacerbated by potential instability of the ligand where both the imine linkage and acetal groups are susceptible to further reaction. Current work is aimed at synthesizing derivatives of $[L^1]^{3-}$, especially with longer chain lengths between the bridgehead N atom and the imine donor atoms, and with saturated amine chains in place of the imine linkers. It is envisaged that these larger and/or more flexible ligands will lead to more stable binuclear complexes. Such complexes might also allow us to examine any correlation[9] between $\mathrm{Ln}\cdots\mathrm{M}$ distance and magnetic exchange interactions.

Acknowledgements

We are grateful to the EPSRC for funding a diffractometer and for a postdoctoral fellowship (to S. P.), and to the University of Edinburgh for a studentship (to S. J. A.).

References

1 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225; V. McKee, *Adv. Inorg. Chem.*, 1993, **40**, 323; D. E. Fenton and H. Okawa, in *Perspectives in Coordination Chemistry*, eds. A. F. Williams, C. Floriani and A. E. Merbach, VCH, Weinheim, 1992, p. 203; K. K. Nanda, L. K. Thompson, J. N. Brisdon and K. Nag, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1337; K. K. Nanda, R. Das, L. K. Thompson, K. Vewnkatsubrammanian, P. Paul and K. Nag, *Inorg. Chem.*, 1994, **33**, 1188; A. J. Atkins, D. Black, A. J. Blake, A. Marin-Becerra, S. Parsons, L. Ruiz-Ramirez and M. Schröder, *Chem. Commun.*, 1996, 457.

2 For example, see B. F. Hoskins and G. A. Williams, *Aust. J. Chem.*, 1975, **28**, 2593, 2607; R. R. Gagné, L. M. Henling and T. J. Kistenmacher, *Inorg. Chem.*, 1980, **19**, 1226; R. R. Gagné, C. L. Siro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; R. C. Long and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 1513; S. K. Mandal, L. K. Thompson, K. Nag, J.-P. Charland and E. Gabe, *Inorg. Chem.*, 1987, **26**, 1391; D. Luneau, J.-M. Savariault, P. Cassoux and J.-P. Tuchagues, *J. Chem. Soc., Danton Trans.*, 1988, 1225; V. McKee and S. S. Tandon, *J. Chem. Soc., Chem Commun.*, 1988, 385; M. Tadokoro, H. Sakiyama, N. Matsumoto, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3337; M. Tdokoro, H. Okawa, N. Matsumoto, M. Koikawa and S. Kida, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 1657; M. Tadokoro, H. Sakiyama, N. Matsumoto, M. Kodera, H. Okawa and S. Kida, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 313; R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073; H.-R. Chang, S. K. Larsen, P. D. W. Boyd, C. G. Pierpont and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1988, **110**, 4565; D. G. McCollum, L. Hall, C. White, R. Ostrander, A. L. Rheingold, J. Whelan and B. Bosnich, *Inorg. Chem.*, 1994, **33**, 924; J. Nishio, H. Okawa, S.-I. Ohtsuka and M. Tomono, *Inorg. Chim. Acta*,1994, **218**, 27; C. Fraser, R. Ostrander, A. L. Rheingold, C. White and B. Bosnich, *Inorg. Chem.*, 1994, **33**, 324.

3 H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **45**, 1759; T. Aono, H. Wada, Y. Aratake, N. Matsumoto, H. Okawa and Y. Matsuda, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 25; M. Sakamoto, Y. Nishida, K. Ohhara, Y. Sadaoka, A. Matsumoto and H. Okawa, *Polyhedron*, 1995, **14**, 2505; Sh Ohtsuka, M. Kodera, K. Motoda, M. Ohba and H. Okawa, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2599.

4 J.-P. Costes, F. Dahan, A. Dupuis and J.-P. Laurent, *Inorg. Chem.*, 1996, **35**, 2400.

5 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128; A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1986, **25**, 572; C. Benelli, A. Caneschi, D. Gatteschi, O. Giullou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1751.

6 A. J. Blake, P. E. Y. Milne, P. Thornton and R. E. P. Winpenny, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **31**, 1139; A. J. Blake, P. E. Y. Milne and R. E. P. Winpenny, *J. Chem. Soc.*, *Dalton Trans.*, 1993, 3727; A. J. Blake, V. A. Cherepanov, A. A. Dunlop, C. M. Grant, P. E. Y. Milne, J. M. Rawson and R. E. P. Winpenny, *J. Chem. Soc.*, *Dalton Trans.*, 1994, 2719.

7 M. Andruh, I. Ramade, E. Codjovi, O. Giullou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822.

8 S. Wang, S. J. Trepanier and M. J. Wagner, *Inorg. Chem.*, 1993, **32**, 833.

9 A. J. Blake, C. Benelli, P. E. Y. Milne, J. M. Rawson and R. E. P. Winpenny, *Chem. Eur. J.*, 1995, **1**, 614.

10 S. Liu, L.-W. Yang, S. J. Rettig and C. Orvig, *Inorg. Chem.*, 1993, **32**, 2773.

11 K. A. O. Chin, J. R. Morrow, C. H. Lake and M. R. Churchill, *Inorg. Chem.*, 1994, **33**, 656.

12 N. Sabbatini, M. Guardigli and J.-M. Lehn, *Coord. Chem. Rev.*, 1993, **123**, 201 and refs. therein.

13 A. J. Amoroso, A. M. Cargill Thompson, J. C. Jeffery, P. L. Jones, J. A. McCleverty and M. D. Ward, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 2571.

14 S. J. Archibald, A. J. Blake, M. Schröder and R. E. P. Winpenny, *J. Chem. Soc.*, *Chem. Commun.*, 1994, 1669.

15 R. R. Gagné, C. L. Spiro, T. J. Smith, C. A. Hamann, W. R. Thies and A. K. Shiemke, *J. Am. Chem. Soc.*, 1981, **103**, 4073.

16 J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105.

17 W. Clegg, *Acta Crystallogr.*, *Sect. A*, 1981, **37**, 22.

18 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr.*, *Sect. A*, 1968, **24**, 351.

19 P. T. Buerskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. Van den Hark, P. A. J. Prick, J. H. Noordik, G. Buerskens, V. Parathasarathi, H. J. Bruins-Slot, R. C. Haltiwanger, M. K. Strumpel and J. M. M. Smits, *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Clarenden Press, Oxford, 1985, pp. 216–226.

20 G. M. Sheldrick, SHELXS 86, University of Göttingen, 1986.

21 G. M. Sheldrick, SHELXL 93, University of Göttingen, 1993.

22 D. J. Watkin, C. K. Prout, J. R. Carruthers and P. W. Betteridge, CRYSTALS, Issue 10, Chemical Crystallography Laboratory, University of Oxford, 1996.

23 M. D. Timken, W. A. Marritt, D. N. Hendrickson, R. A. Gagné and E. Sinn, *Inorg. Chem.*, 1985, **24**, 4202.

24 O. W. Howarth, Q. Lu, J. F. Malone, D. J. Marrs, N. Martin, V. McKee and J. Nelson, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 1739 and refs. therein.

25 For example, see J. R. Oscarson, J. Bordner, W. D. Celmer, W. P. Cullen, L. H. Huang, H. Maeder, P. M. Moshier, S. Nishiyama, L. Presseau, R. Shibakawa and J. Tone, *J. Antibiot.*, 1989, **42**, 37; J. P. Dirlam, L. Presseau-Linabury and D. A. Koss, *J. Antibiot.*, 1990, **43**, 727; Y. Takahashi, H. Nakamura, R. Ogata, N. Matsuda, M. Hamada, H. Naganawa, T. Takita, Y. Iitaka, K. Sato and T. Takeuchi, *J. Antibot.*, 1990, **43**, 441.

26 For example, see M. Pinkerton and L. K. Steinrauf, *J. Mol. Biol.*, 1970, **49**, 533; J. F. Blount, R. H. Evans, jun., C.-M. Liu, T. Hermann and J. W. Westley, *J. Chem. Soc.*, *Chem. Commun.*, 1975, 853; H. Koyama and K. Utsumi-Oda, *J. Chem. Soc.*, *Perkin Trans. 2.*, 1977, 1531.

27 J. J. Daly, F. Sanz, R. P. A. Sneeden and H. H. Zeiss, *Helv. Chim. Acta*, 1974, **57**, 1863; H. W. Roesky, E. Peymann, J. Schimkowiak, M. Noltmeyer, W. Pinkert and G. M. Sheldrick, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 981; P. G. Jones, H. W. Roesky, J. Liebermann and G. M. Sheldrick, *Z. Noturforsch.*, *Teil. B*, 1984, **39**, 1729; G. R. Newkome, H. C. R. Taylor, F. R. Fronczek and V. K. Gupta, *J. Org. Chem.*, 1986, **51**, 970; *Inorg. Chem.*, 1986, **25**, 1149; E. Lindner, J. Dettinger, H. A. Mayer, H. Kuhbauch, R. Fawzi and M. Steimann, *Chem. Ber.*, 1993, **126**, 1317; E. Lindner, J. Dettinger, R. Fawzi and M. Steimann, *Chem. Ber.*, 1993, **126**, 1347.

28 P. D. Brotherton, D. Wege, A. H. White and E. N. Maslen, *J. Chem. Soc., Dalton Trans.*, 1974, 1876; Y. Barbay, J. Loset, R. Roulet and G. Chapuis, *Helv. Chim. Acta*, 1986, **69**, 195; D. M. Walba, M. Hermsmeier, R. C. Haltiwanger and J. H. Noordik, *J. Org. Chem.*, 1986, **51**, 245; S. J. Angyal, D. C. Craig, J. Defaye and A. Gadelle, *Can. J. Chem.*, 1990, **68**, 1140; Y. Takai, Y. Okumura, T. Tanaka, M. Sawada, S. Takahashi, M. Shiro, M. Kawamura and T. Uchiyama, *J. Org. Chem.*, 1994, **59**, 2967.

Received 23*rd July* 1996; *Paper* 6/05154E