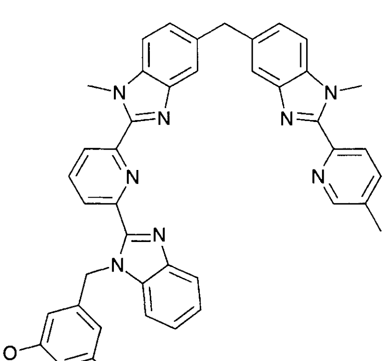
The First Structurally Characterized and Strongly Luminescent Self-assembled Helical Heterodinuclear d–f Complex

Claude Piguet,*[a] Gérald Bernardinelli,[b] Jean-Claude G. Bünzli,[c] Stéphane Petoud[c] and Gérard Hopfgartner[d]

[a] *Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai E. Ansermet, CH-1211 Geneva 4, Switzerland*
[b] *Laboratory of X-ray Crystallography, University of Geneva, 24 quai E. Ansermet, CH-1211 Geneva 4, Switzerland*
[c] *Institute of Inorganic and Analytical Chemistry, University of Lausanne, BCH, CH-1015 Lausanne, Switzerland*
[d] *F. Hoffmann-La Roche Ltd., Pharma Division, Department of Drug Metabolism and Kinetics, Bioanalytical Section, CH-4002 Basel, Switzerland*

The new segmental ligand L^2, which possesses a terminal *N,N′*-diethylcarboxamido group, reacts with Eu^{III} and Zn^{II} to give the highly stable and strongly luminescent self-assembled helical heterodinuclear d–f complex $[EuZn(L^2)_3]^{5+}$.

The selective synthesis of organized homopolynuclear supramolecular complexes by the assembly of segmental ligands with labile metal ions is a theme of considerable current interest.[1–7] Double-[1] and triple-helical,[2] cylindrical[3] and toroidal[4] complexes have been investigated to unravel the mechanism of the assembly processes eventually leading to the design of extended homonuclear inorganic architectures such as grids,[5] racks[6] and organometallic catenates.[7] However, little attention has been devoted to the development of segmental ligands with binding sites coded for the selective complexation of different metal ions.[8] Heteronuclear double-helicates[9] and organometallic [2]-catenates[10] have been prepared by using segmental ligands possessing multidentate heterocyclic units. The formation of triple-helical d–f complexes $[LnM(L^1)_3]^{5+}$ (M = Zn[11], Fe[12]) in solution has demonstrated the potentiality of this approach for the design of new lanthanide-containing building blocks with controlled magnetic and photophysical properties.[12] However, $[EuZn(L^1)_3]^{5+}$ is only weakly luminescent as a result of the closely packed arrangement of the ligands[13] and requires concentrations larger than 10^{-2} mol dm^{-3} to be formed quantitatively in acetonitrile.[11,12] The replacement of the terminal benzimidazole group of L^1 by a *N,N′*-diethylcarboxamido group in L^2 will affect both the selectivity of the assembly process and the quantum yield of the heterodinuclear complexes since carboxamido groups have a high affinity for Ln^{III} ions[14] and favour resonant $L^2 \rightarrow Ln^{III}$ (Ln = Eu, Tb) energy transfers.[15]



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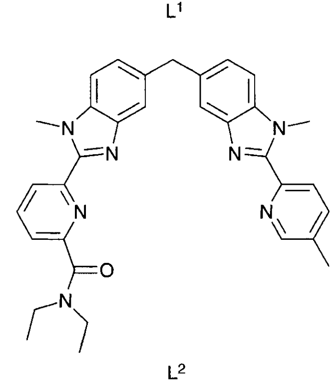

L²

Electrospray mass spectrometric (ES-MS) and spectrophotometric titrations of 2-[6-(*N,N′*-diethylcarboxamido)pyridin-2-yl]-1,1′-dimethyl-5,5′-methylene-2′-(5-methylpyridin-2-yl)-bis[1*H*-benzimidazole] (L^2) 10^{-4} mol dm^{-3} in acetonitrile with an equimolar mixture of $Eu(ClO_4)_3{\cdot}7H_2O$ and $Zn(ClO_4)_2{\cdot}6H_2O$ {M : L^2 = 0.1–1.2 : 1, [M] = [Eu] = [Zn]} show the formation of $[EuZn(L^2)_3]^{5+}$ {*m/z* 369.8, together with its adduct ions $[EuZn(L^2)_3(ClO_4)_n]^{(5-n)+}$, n = 1–3}[4] as the only significant complex species. In comparison, only 45% of $[EuZn(L^1)_3]^{5+}$ is formed under the same conditions.[11] The spectrophotometric data can be fitted to eqn. (1) with log β_1 = 29.0(8) and a rms difference of 0.002.

$$Zn^{2+} + Eu^{3+} + 3L^2 \leftrightarrow [EuZn(L^2)_3]^{5+} \qquad (1)$$

For $[EuZn(L^1)_3]^{5+}$, log β_1 was equal to 25.3(4) under the same experimental conditions.[11]

The ^{1}H NMR spectrum of $[EuZn(L^2)_3]^{5+}$ displays 23 sharp signals corresponding to three equivalent head-to-head[9] ligands wrapped about the Eu–Zn axis and producing a C_3 structure on the NMR timescale, as confirmed by intrastrand [C(8)–H : C(15)–H, C(8)–H : C(13)–H, C(13)–H : C(15)–H] and interstrand [C(33b)–H : C(10c)–H, C(18b)–H : C(11c)–H, C(19b)–H : C(32c)–H, C(30a)–H : C(33b)–H] NOE effects[11,12] and AB spin systems for the diastereotopic methylene protons of C(13), C(27) and C(29).[1] Slow diffusion of diethyl ether into a concentrated acetonitrile solution leads to the quantitative isolation of a polycrystalline aggregate whose elemental analysis corresponds to $[EuZn(L^2)_3][ClO_4]_5{\cdot}0.5Et_2O{\cdot}2H_2O$ **1**. Fragile colourless single crystals of $[EuZn(L^2)_3][ClO_4][CF_3SO_3]_4{\cdot}3.5MeCN$ **2** suitable for X-ray diffraction analyses were obtained by diffusion of diisopropyl ether into an acetonitrile solution of **1** containing 30 equiv. of $NBu_4CF_3SO_3$, followed by ultrasonic mixing and slow cooling to 277 K.

A stereoscopic view of the $[EuZn(L^2)_3]^{5+}$ cation [Fig. 1(*b*)]† shows the three ligands wrapped around a pseudo-C_3 axis passing through the metal ions [Eu···Zn 8.960(3) Å]. The helical twist of the ligands L^2 is achieved by rotation about the interannular C–C bonds (interplane angles: 3–40°) and by spiralling around the C(9)–C(13) and C(13)–C(14) bonds of the spacer, which brings the two connected benzimidazole groups almost perpendicular to each other (interplane angles: 81–85°) as found for homodinuclear triple-helical complexes with the same diphenylmethane spacer.[16] The tridentate units are meridionally three-coordinated to Eu^{III} and adopt bent conformations with Eu^{III} located significantly out of the plane of the coordinated pyridine rings [0.77–1.24 Å, Fig. 1(*b*)]. The coordination polyhedron of the Eu atom is a slightly distorted tricapped trigonal prism with the three N atoms of the benzimidazole units and the three O atoms occupying the vertices of the prism. The three N atoms of the pyridine units occupy the capping positions and form an intermediate plane almost containing the Eu atoms (deviation: 0.13 Å toward Zn). The Eu–O and Eu–N bond distances are close to the standard values reported for Eu–O(amide),[17] Eu–N(pyridine) and Eu–

N(benzimidazole).[2,13] Zn^{II} lies in a severely distorted octahedral site produced by the six N donor atoms of the three bidentate units. The Zn–N(1c) bond length [2.52(2) Å] is much longer than the standard Zn–N(pyridine) value (2.111 Å)[18] and deviates from the average Zn–N distance in **2** (2.17 Å). As expected from the thermodynamic '*trans* influence',[19] the Zn–N(2b) bond [*trans* to Zn–N(1c)] is short [2.01(2) Å] which shifts N(1a) and N(2c) toward N(1c) [N(1a)–Zn–N(2c) 158.8(6)°, Fig. 1)] leading to a zinc coordination sphere close to a distorted trigonal-bipyramid [if the loosely bound N(1c) atom is neglected]. The distortion results from a close intermolecular packing of the $[EuZn(L^2)_3]^{5+}$ cations by pairs in the unit cell. Within each pair, the cations are related by an inversion centre and adopt a staggered head-to-head arrangement leading to (*i*) parallel pseudo-C_3 axes, (*ii*) a close contact between the methyl groups of the pyridine rings belonging to different cations and (*iii*) a short intermolecular Zn···Zn distance [8.314(3) Å].

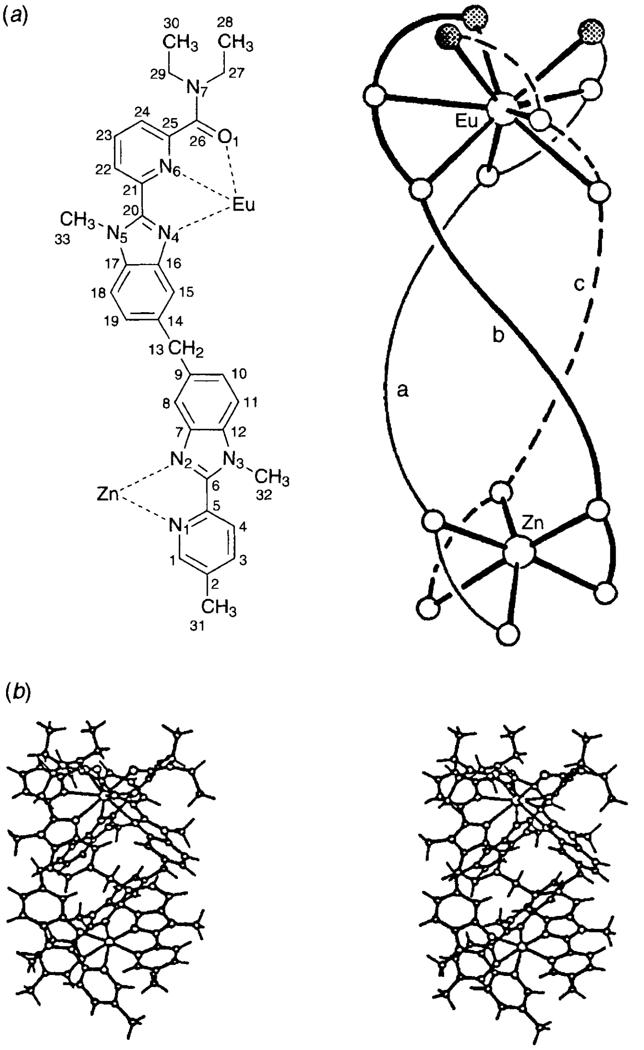

Fig. 1 (*a*) Atomic numbering scheme for $[EuZn(L^2)_3]^{5+}$ and (*b*) ORTEP stereoview[24] of the cation $[EuZn(L^2)_3]^{5+}$ perpendicular to the pseudo-C_3 axis in **2**. Selected bond lengths (Å) and angles (°): Eu···Zn 8.960(3), Eu–O(1a) 2.39(1), Eu–N(4a) 2.52(2), Eu–N(6a) 2.59(2), Eu–O(1b) 2.37(1), Eu–N(4b) 2.58(1), Eu–N(6b) 2.64(1), Eu–O(1c) 2.38(1), Eu–N(4c) 2.60(2), Eu–N(6c) 2.55(2), Zn–N(1a) 2.14(1), Zn–N(2a) 2.12(2), Zn–N(1b) 2.19(2), Zn–N(2b) 2.01(2), Zn–N(1c) 2.52(2), Zn–N(2c) 2.03(2), O(1a)–Eu–N(6a) 64.1(5), O(1b)–Eu–N(6b) 63.5(4), O(1c)–Eu–N(6c) 64.1(5), N(4a)–Eu–N(6a) 63.5(5), N(4b)–Eu–N(6b) 63.1(5), N(4c)–Eu–N(6c) 62.5(5), N(6a)–Eu–N(6b) 117.5, N(6a)–Eu–N(6c) 120.6(5), N(6b)–Eu–N(6c) 121.2(5), N(1a)–Zn–N(2a) 78.5(6), N(1b)–Zn–N(2b) 76.7(6), N(1c)–Zn–N(2c) 73.9(6), N(1a)–Zn–N(1b) 96.3(6), N(1a)–Zn–N(1c) 85.0(5), N(1b)–Zn–N(1c) 97.5(6), N(2a)–Zn–N(2b) 105.6(6), N(2a)–Zn–N(2c) 95.9(6), N(2b)–Zn–N(2c) 104.7(6).

The free ligand displays a broad structured luminescence band at 77 K centred at 24 940 cm^{-1} ($^1\pi\pi^*$), with two weak shoulders at 20 040 and 18 870 cm^{-1} corresponding to the emission from the triplet states ($^3\pi\pi^*$) of the two coordinating regions of the ligand[12] [lifetimes: 559(15) and 40(2) ms at 10 K). Excitation of **1** at 10 K through the ligand $^1\pi\pi^*$ level (25 315 cm^{-1}) gives only sharp emission peaks arising from Eu($^5D_0$) level. The laser-excited excitation spectrum of the $^5D_0 \leftarrow {}^7F_0$ transition displays one major component at 17 232 cm^{-1} together with a weak shoulder around 17 224 cm^{-1} (full width at half height 12 cm^{-1}), a situation commonly observed for polycrystalline aggregates.[13] Selective laser excitation of the $^5D_0 \leftarrow {}^7F_0$ transition profile provides very similar emission spectra typical of slightly distorted C_3 species ($^7F_1$ crystal field levels at 287, 407 and 449 cm^{-1} for λ_{exc} = 17 232 cm^{-1})[11–13] in agreement with the crystal structure of **2**. Under excitation at 25 315 cm^{-1} (ligand $^1\pi\pi^*$ level), the corrected and integrated intensities of the transitions $^5D_0 \rightarrow {}^7F_j$ amount to 0.01, 1.0, 1.6, 0.09 and 1.8 for j = 0,1,2,3 and 4 respectively pointing to a geometry around Eu^{III} close to the ideal D_{3h} symmetry [weak hypersensitive $^5D_0 \rightarrow {}^7F_2$ transition and small splitting between the two low-energy components of the $^5D_0 \rightarrow {}^7F_1$ transition (42 cm^{-1})].[20] Although less intense, the emission spectra of **1** at 295 K in the solid state and in acetonitrile solution (10^{-3} and 10^{-4} mol dm^{-3}) (Fig. 2) are not strongly altered which indicates that the triple-helical structure of $[EuZn(L^2)_3]^{5+}$ is maintained in solution, in agreement with NMR data. The lifetimes of the Eu($^5D_0$) level in the solid state [2.19(1) ms at 10 K, 1.67(2) ms at 295 K] and in acetonitrile solution at 295 K [2.84(5) ms (10^{-4} mol dm^{-3}), 2.59(1) ms (10^{-3} mol dm^{-3})] point to an Eu^{III} ion well protected from quenching processes[20] by the L^2 ligands. Quantum yield data in acetonitrile‡ (Table 1) show that $[EuZn(L^2)_3]^{5+}$ is more luminescent than $[EuZn(L^1)_3]^{5+}$ by a factor 10^3 to 10^4. This striking increase is attributed to the presence of the carboxamido groups which remove the helical close packing of the tridentate units around Eu^{III} (ref. 13) and allow an efficient energy transfer between the ligand feeding levels and the Eu($^5D_0$) emitting level (antenna effect).[15]

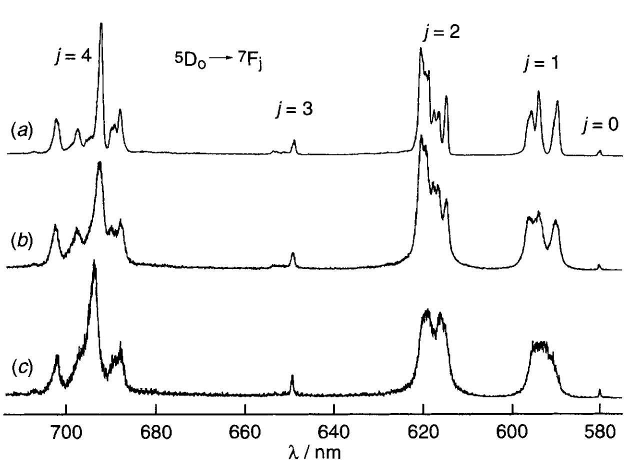

Fig. 2 Luminescence spectra of $[EuZn(L^2)_3][ClO_4]_5$ in the solid state at (*a*) 10 K, (*b*) 295 K and (*c*) in acetonitrile solution (295 K, 10^{-3} mol dm^{-1}), λ_{exc} = 395 nm. Vertical scale: arbitrary units.

Table 1 Quantum yields at 295 K for anhydrous acetonitrile solutions relative to $[Eu(terpy)_3]^{3+}$ (terpy = 2,2′;6′,2″-terpyridine)

Compound	c/mol dm^{-3}	λ_{exc}/nm	η_{rel}
$[Eu(terpy)_3]^{3+}$	1×10^{-3}	390	1.0
$[EuZn(L^1)_3]^{5+}$	1×10^{-3}	440	$< 10^{-4}$
$[EuZn(L^2)_3]^{5+}$	1×10^{-3}	395	0.13
	1×10^{-4}	380	0.29

In conclusion, the substitution of the terminal benzimidazole group of L^1 by a *N,N′*-diethylcarboxamido group in L^2 (*i*) significantly increases the quantum yield of the resulting heterodinuclear complex $[EuZn(L^2)_3]^{5+}$, (*ii*) improves the selectivity of the assembly process and (*iii*) leads to the formation of crystalline materials in the solid state, in contrast with the systematic isolation of amorphous powders for the complexes of L^1.[11,12] In view of the long Eu($^5D_0$) lifetime and the large quantum yield measured for $[EuZn(L^2)_3]^{5+}$, it appears that the bulky terminal benzimidazole group of L^1 is not crucial for the protection of Eu^{III} from quenching processes. Strongly luminescent self-assembled heterodinuclear d–f complexes may be thus designed from sterically less constrained segmental ligands such as L^2.

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Footnotes

† *Crystal Data* for $[EuZn(L^2)_3][ClO_4][CF_3SO_3]_4 \cdot 3.5CH_3CN$ **2**, $C_{110}H_{109.5}ClEuF_{12}N_{24.5}O_{19}S_4Zn$ M = 2687.7, monoclinic, space group $C2/c$, a = 50.417(8), b = 20.822(4), c = 23.498(5) Å, β = 92.67(1)°, U = 24641(8) Å^3 (by least-squares refinement of 29 reflections, $38 \leqslant 2\theta \leqslant 60°$), Z = 8, D_c = 1.46 g cm^{-3}, $F(000)$ = 11088. Colourless prisms. Crystal dimensions 0.10 × 0.25 × 0.28 mm, μ(Cu-Kα) = 5.472 mm^{-1}.

Nonius CAD4 diffractometer, T = 200 K, ω–2θ scan, scan width = 1.05 + 0.14 tanθ, scan speed 0.137° s^{-1}, Cu-Kα radiation (λ = 1.5418 Å); 13029 reflections measured ($4 \leqslant 2\theta \leqslant 100°$, $-50 < h < 50$, $0 < k < 20$, $0 < l < 23$), 12641 unique reflections (R_{int} for equivalent reflections = 0.102) of which 7796 were observable $[|F_0| > 4\sigma(F_0)]$. Two reference reflections were measured every 30 min and showed a total decrease in intensity of 5.4% and all intensities were corrected for this drift. Data were corrected for Lorentz, polarization and absorption effects[21] (A^*_{min} = 1.725, A^*_{max} = 4.387). The structure was solved by direct methods using MULTAN 87;[22] all other calculations used XTAL[23] system and ORTEP II[24] programs. Refinements (on F) were performed with four blocked matrices (ligand a, Eu, Zn; ligand b; ligand c; perchlorate, triflates and solvent molecules). The non-H atoms of the solvent molecules and the four O atoms of the perchlorate were refined with isotropic displacement parameters (16 atoms) and all the other atoms (176) with anisotropic displacement parameters. The perchlorate and one triflate anion are disordered and were refined with respectively seven O atom and four F atom positions. Sets of three atoms in each of four sites were interpreted as acetonitrile molecules. Final R and R' = 0.099 (w = 1). H atoms were placed in calculated positions and contributed to F_c calculations. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ The relative quantum yields were calculated using the following formula[13] $Q_x/Q_r = \langle A_r(\lambda_r)/A_x(\lambda_x)\rangle \langle I(\lambda_r)/I(\lambda_x)\rangle \langle n^2_x/n^2_r\rangle \langle D_x/D_r\rangle$ where subscript r stands for the reference and x for the sample; A is the absorbance at the excitation wavelength, I is the intensity of the excitation light at the same wavelength, n is the refractive index (1.341 for all the solutions) and D is the integrated intensity.

References

1 E. C. Constable, *Tetrahedron*, 1992, **48**, 10013 and references therein.

2 C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, G. Hopfgartner and A. F. Williams, *J. Am. Chem. Soc.*, 1993, **115**, 8197 and references therein.

3 P. Baxter, J.-M. Lehn, A. DeCian and J. Fischer, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 69.

4 G. Hopfgartner, C. Piguet and J. D. Henion, *J. Am. Soc. Mass Spectrom.*, 1994, **5**, 748; J. Wojaczynski and L. Latos-Grazynski, *Inorg. Chem.*, 1995, **34**, 1044.

5 P. Baxter, J.-M. Lehn, J. Fischer and M.-T. Youinou, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2284.

6 H. Sleiman, P. Baxter, J.-M. Lehn and K. Rissanen, *J. Chem. Soc., Chem. Commun.*, 1995, 715; J.-C. Chambron, C. Dietrich-Buchecker, J.-F. Nierengarten, J.-P. Sauvage, N. Solladié, A.-M. Albrecht-Gary and M. Meyer, *New J. Chem.*, 1995, **19**, 409.

7 M. Fujita, F. Ibukoro, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 4175.

8 C. Piguet, B. Bocquet and G. Hopfgartner, *Helv. Chim. Acta*, 1994, **77**, 931.

9 C. Piguet, G. Hopfgartner, B. Bocquet, O. Schaad and A. F. Williams, *J. Am. Chem. Soc.*, 1994, **116**, 9092; E. C. Constable, A. J. Edwards, P. R. Raithby and J. V. Walker, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1465.

10 C. Piguet, G. Bernardinelli, A. F. Williams and B. Bocquet, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 582.

11 C. Piguet, G. Hopfgartner, A. F., Williams and J.-C. G. Bünzli, *J. Chem. Soc., Chem. Commun.*, 1995, 491. C. Piguet, E. Rivara-Minten, G. Hopfgartner and J.-C. G. Bünzli, *Helv. Chim. Acta*, 1995, **78**, 1541.

12 C. Piguet, E. Rivara-Minten, G. Hopfgartner and J.-C. G. Bünzli, *Helv. Chim. Acta*, 1995, **78**, 1651.

13 C. Piguet, J.-C. G. Bünzli, G. Bernardinelli, C. G. Bochet and P. Froidevaux, *J. Chem. Soc., Dalton Trans.*, 1995, 83.

14 C. Paul-Roth and K. N. Raymond, *Inorg. Chem.*, 1995, **34**, 1408.

15 N. Sabbatini, M. Guardigli, A. Mecati, V. Balzani, R. Ungaro, E. Ghildini, A. Casnati and A. Pochini, *J. Chem. Soc., Chem. Commun.*, 1990, 878; P. A. Brayshaw, J.-C. G. Bünzli, P. Froidevaux, J. M. Harrowfield, Y. Kim and A. N. Sobolev, *Inorg. Chem.*, 1995, **34**, 2068.

16 C. Piguet, G. Bernardinelli and A. F. Williams, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 1621; C. Piguet, G. Bernardinelli, B. Bocquet, O. Schaad and A. F. Williams, *Inorg. Chem.*, 1994, **33**, 4112.

17 S. J. Franklin and K. N. Raymond, *Inorg. Chem.*, 1994, **33**, 5794.

18 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

19 T. G. Appleton, H. C. Clark and L. E. Maurer, *Coord. Chem. Rev.*, 1973, **10**, 335.

20 J.-C. G. Bünzli, in *Lanthanide Probes in Life, Chemical and Earth Sciences*, ed. G. R. Choppin and J.-C. G. Bünzli, Elsevier Science Publ. Co., Amsterdam, 1989, ch. 7.

21 E. Blanc, D. Schwarzenbach and H. D. Flack, *J. Appl. Crystallogr.*, 1991, **24**, 1035.

22 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, D. Germain, J. P. Declercq and M. M. Woolfson, MULTAN 87, Universities of York, England, and Louvaine-La-Neuve, Belgium, 1987.

23 XTAL 3.2 User's Manual, ed. S. R. Hall and J. M. Stewart, Universities of Western Australia and Maryland, 1992.

24 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.