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Heterotrinuclear complexes containing d- and f-block elements: synthesis and structural characterisation of novel lanthanide(III)–nickel(II)–lanthanide(III) compounds bridged by oxamidate

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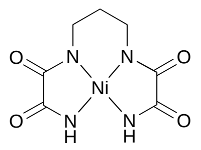
The reaction of lanthanide(III) ions with a tripodal ligand $HB(pz)_3^-$ [= hydrotris(pyrazol-1-yl)borate] and a 'complex ligand' $[NiL]^{2-}$ [L = tdo^{4-} or edo^{4-}, where H_4tdo = trimethylenebis(oxamide) and H_4edo = ethylenebis(oxamide)] in aqueous solution produced the novel 3d–4f heterotrinuclear complexes $[NiL\{Ln[HB(pz)_3]_2\}_2]$ [abbreviated as Ni(tdo)Ln_2 (Ln = Eu, Tb or Yb) and Ni(edo)Ln_2 (Ln = Sm to Lu)]. The crystal structures of Ni(tdo)Yb_2 and Ni(edo)Lu_2 have been determined by X-ray diffraction method. The Ni atoms in both have a square-planar environment and the Ln atoms have eight-co-ordinated square-antiprismatic co-ordination geometries.

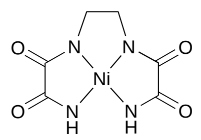
For two decades or so a large number of investigations of heteropolymetallic compounds have been described.[1] The studies of these compounds have often been performed in relation to either modelling of some metalloenzymes containing several kinds of metal ions or to design novel molecular materials. In particular much attention has been paid to compounds including both transition-metal and lanthanide ions because they are possible precursors and/or models of magnetic materials. Especially, as models for high-temperature superconducting ceramics, copper(II)–lanthanoid(III) complexes have been extensively studied.[2–10] In contrast complexes containing other transition-metal ions are scarce, but a few characterised ones have interesting structures.[11–15] For example, Piguet *et al.*[16] investigated the self-assembled triple-stranded complexes $[Ln^{III}Fe^{II}L_3]^{5+}$ {L = 2-[6-(diethylcarbamoyl)pyridin-2-yl]-1,1′-dimethyl-2′-(5-methylpyridin-2-yl)-5,5′-methylenebis(1*H*-benzimidazole)}. They discovered that these complexes show iron(II) spin crossover around room temperature. Winpenny and co-workers[17] reported the tetranuclear complexes $[Co^{II}_2Ln^{III}_2(OH)(chp)_6(NO_3)_5]^{2-}$ (chp = 6-chloro-2-pyridonate) in which the two cobalt sites are quite distinct, one having a tetrahedral geometry and the other in a distorted octahedral arrangement. In this way 3d–4f heteropolynuclear complexes provide a variety of interesting structural information. However, there is no study on discrete linear 4f–3d–4f heterotrinuclear complexes.

Two synthetic methods are available for discrete heterotrinuclear complexes: (1) the use of heterotrinucleating ligands with some dissimilar co-ordination sites and (2) the use of 'complex ligands' that can function as ligands to the second metal ion. We chose the latter synthetic approach using $[Ni(tdo)]^{2-}$ and $[Ni(edo)]^{2-}$, where H_4tdo = trimethylenebis(oxamide) and H_4edo = ethylenebis(oxamide). These 'complex ligands' have two free O,O′ sites which might form a novel type of Ln^{III}–Ni^{II}–Ln^{III} heterotrinuclear complexes with the tripodal ligand $HB(pz)_3^-$ [= hydrotris(pyrazol-1-yl)borate] since a series of stable complexes containing the $\{Ln[HB(pz)_3]_2\}^+$ moiety could be prepared using O,O′ didentate uninegative coligands to complete the co-ordination shell of the lanthanide(III) ions as reported by Moss and Jones.[18–20]

This paper describes the successful synthesis and characterisation of two series of new 3d–4f heterotrinuclear complexes, $[Ni(tdo)\{Ln[HB(pz)_3]_2\}_2]$ [abbreviated Ni(tdo)Ln_2; Ln = Eu, Tb or Yb] and $[Ni(edo)\{Ln[HB(pz)_3]_2\}_2]$ [abbreviated Ni(edo)Ln_2; Ln = Sm to Lu]. The crystal structures of Ni(tdo)Yb_2 and Ni(edo)Lu_2 are reported.



$[Ni(tdo)]^{2-}$



$[Ni(edo)]^{2-}$

Experimental

Syntheses

Lanthanide trichloride hexahydrates and triacetate tetrahydrates were from Wako Pure Chemical Industries Ltd. Sodium hydrotris(pyrazol-1-yl)borate was prepared by the literature method,[21] as were the salts $Na_2[Ni(tdo)]\cdot 4H_2O$ and $Na_2[Ni(edo)]\cdot H_2O$.[22]

$[Ni(tdo)\{Ln[HB(pz)_3]_2\}_2]$ [Ni(tdo)Ln_2; Ln = Eu, Tb or Yb]. These complexes were prepared by the same method, therefore only the synthesis of one of them, namely Ni(tdo)Yb_2, is detailed. Aqueous solutions (15 cm^3) of $Na[HB(pz)_3]$ (0.20 g, 0.8 mmol) and $Na_2[Ni(tdo)]\cdot 4H_2O$ (0.078 g, 0.2 mmol) were added to a stirred solution of $YbCl_3\cdot 6H_2O$ (0.15 g, 0.4 mmol) in water (20 cm^3). The stirring was continued for 10 min. Then the mixture was cooled in a refrigerator overnight. The yellow precipitate was filtered off, washed three times with water and dried under vacuum. The crude product was recrystallised several times from dichloromethane–hexane. A single crystal suitable for X-ray analysis was obtained by slow evaporation of a solution of the complex in dichloromethane–acetonitrile. The complexes of Eu^{III} and Tb^{III} were prepared similarly using the appropriate lanthanide trichloride hexahydrates.

$[Ni(edo)\{Ln[HB(pz)_3]_2\}_2]$ [Ni(edo)Ln_2; Ln = Sm to Lu]. These complexes were obtained by the method for Ni(tdo)Ln_2 using $Na_2[Ni(edo)]\cdot H_2O$ instead of $Na_2[Ni(tdo)]\cdot 4H_2O$; $LnCl_3\cdot 6H_2O$ (Ln = Eu, Tb or Yb) or $Ln(CH_3CO_2)_3\cdot 4H_2O$ (Ln = Sm, Gd, Dy, Ho, Er, Tm or Lu) was used as lanthanide source.

Measurements

Infrared spectra were recorded on a Shimadzu IR-435 spectrophotometer using Nujol mulls, ^1H NMR spectra using a JEOL JNM-EX-270 FT spectrometer at 25 °C in $CDCl_3$ with $SiMe_4$ as the internal reference, luminescence and FAB mass spectra with Perkin-Elmer LS50B and JEOL JMS-SX102 spectrometers, respectively. Magnetic susceptibility data were collected on a microcrystalline sample of Ni(edo)Gd_2 with use of a SQUID-based sample magnetometer on a QUANTUM Design model MPMS instrument. All data were corrected for diamagnetic susceptibilities of the ligand estimated from Pascal's constants [-4.38×10^{-4} cm^3 mol^{-1} for Ni(edo)Gd_2].

Crystallography

Yellow plate crystals of Ni(tdo)Yb_2 and yellow prismatic crystals of Ni(edo)Lu_2 were grown from a mixture of dichloromethane and acetonitrile. Crystals suitable for X-ray diffraction [approximate dimensions $0.80 \times 0.60 \times 0.30$ mm for Ni(tdo)Yb_2 and $0.40 \times 0.25 \times 0.18$ mm for Ni(edo)Lu_2] were sealed in glass capillaries together with mother liquor to prevent efflorescence. The X-ray intensities were measured at 23 °C with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) on a Rigaku AFC-5R four-circle diffractometer. The 2θ–ω scan technique was employed at a scan rate of 16° min^{-1} in θ and scan widths of $1.31 + 0.35 \tan\theta$ for Ni(tdo)Yb_2 or $1.10 + 0.35 \tan\theta$ for Ni(edo)Lu_2. Final lattice constants were determined by least-squares refinements of the orientation angles of 25 centred reflections in the range $29 \leqslant 2\theta \leqslant 30°$. Three standard reflections were monitored every 150, and gradual decomposition of the crystals was observed during the data collection, the $(|F_o|)_{\text{final}}/(|F_o|)_{\text{initial}}$ values being 93.8 and 95.9% for Ni(tdo)Yb_2 and Ni(edo)Lu_2, respectively. The intensities collected for ($+h$, $+k$, $\pm l$) octants at $2\theta \leqslant 60°$ were corrected for Lorentz-polarisation effects, and linear decay and absorption corrections by means of an empirical ψ-scan method[23] were applied. The observed independent reflections with $I > 3\sigma(I)$ were used for the structural calculations carried out on a SGI Indy workstation using TEXSAN software,[24] and complex neutral atom scattering factors were used.[25]

The space group of Ni(tdo)Yb_2 was uniquely determined by systematic absences to be $P2_1/n$. For Ni(edo)Lu_2 systematic absences indicated uniquely the space group $P2_1/c$. The positions of Ln and Ni atoms were determined by Patterson function analysis using the SHELXS 86 program.[26] The structure was refined on F to minimise the function $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma_c^2(F_o) + (0.010|F_o|)^2$, by full-matrix least squares using anisotropic thermal parameters for all non-hydrogen atoms of the trinuclear complex. Hydrogen atoms of the $HB(pz)_3$ moiety were introduced at theoretical positions and fixed during the structural refinement, but those of the disordered tdo and edo moieties were not included.

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Results and Discussion

Synthetic and spectroscopic studies

The FAB mass spectral data of Ni(tdo)Yb_2 and Ni(edo)Eu_2 are summarised in Table 1. Similar spectra were obtained for all the other complexes. The observation of high-mass peaks corresponding to the presence of trinuclear fragments indicates that the reaction of Na[$HB(pz)_3$] and Na_2[Ni(tdo)]·$4H_2O$ or Na_2[Ni(edo)]·H_2O with lanthanide(III) ions in aqueous solutions yields heterotrinuclear complexes.

In addition to FAB mass spectra, elemental analyses (Table 2) show the formation of trinuclear complexes [Ni(tdo){Ln[$HB(pz)_3$]$_2$}$_2$] (Ln = Eu, Tb or Yb) and [Ni(edo){Ln[$HB(pz)_3$]$_2$}$_2$] (Ln = Sm to Lu). These are soluble in dichloromethane and chloroform, but insoluble in water, alcohol, acetonitrile and n-hexane. When a series of Ni(tdo)Ln_2 were synthesized using lanthanide triacetate tetrahydrates instead of trichloride hexahydrates, pure products were not obtained even after repeating recrystallisations. The new complexes for the larger lanthanide(III) ions (Pr and Nd) are sparingly soluble in polar organic solvents, as found for analogous [Ln{$HB(pz)_3$}$_2$L] (L = didentate uninegative ligand) type complexes.[18,19] The low solubilities of these complexes precluded complete purification. Thus, they were only isolated in crude forms.

Table 1 The FAB mass spectral data of Ni(tdo)Yb_2 and Ni(edo)Eu_2

Complex	m/z	Relative intensity	Fragment *
Ni(tdo)Yb_2	1467	3.41	$[M - H]^+$
	1402	9.50	$[M - Hpz]^+$
	1257	6.48	$[M - HB(pz)_3]^+$
	1110	10.37	$[M - 2HB(pz)_3 + pz]^+$
	1044	4.25	$[M - 2HB(pz)_3]^+$
	963	15.55	$[M - 3HB(pz)_3 + 2pz]^+$
	600	100	$[Yb\{HB(pz)_3\}_2]^+$
Ni(edo)Eu_2	1413	4.32	$[M - H]^+$
	1346	9.72	$[M - Hpz]^+$
	1200	11.66	$[M - HB(pz)_3]^+$
	1054	9.72	$[M - 2HB(pz)_3 + pz]^+$
	987	6.91	$[M - 2HB(pz)_3]^+$
	907	15.55	$[M - 3HB(pz)_3 + 2pz]^+$
	579	100	$[Eu\{HB(pz)_3\}_2]^+$

* M = [NiL{Ln[$HB(pz)_3$]$_2$}$_2$] (L = tdo^{4-} or edo^{4-}).

In Table 2 the characteristic IR bands for the complexes are collected. All of the new complexes give almost identical IR spectra, with strong carbonyl stretching bands at 1604–1640 cm^{-1}; Ni(tdo)Ln_2 and Ni(edo)Ln_2 complexes give only one band at *ca.* 1620 cm^{-1} and two bands at 1604–1613 and 1633–1640 cm^{-1}, respectively. Compared with the carbonyl stretching bands at 1587 and 1583 + 1608 cm^{-1} for Na_2[Ni(tdo)]·$4H_2O$ and Na_2[Ni(edo)]·H_2O, respectively, they were shifted by 20–40 cm^{-1} to higher frequencies for the trinuclear complexes. This may be attributed to co-ordination of the carbonyl oxygens to the lanthanide(III) ions, for the shifts have been used as definite proof of an oxamido-bridge.[27] The wavenumbers of these bands increase with atomic number, *e.g.* from 1604 and 1633 cm^{-1} for Ni(edo)Sm_2 to 1613 and 1640 cm^{-1} for Ni(edo)Lu_2. These small shifts probably result from the lanthanide contraction.

The results of ^1H NMR measurements are summarised in Table 2. All the signals of Ni(edo)Lu_2 are located in the chemical shift regions for diamagnetic compounds. This indicates that Ni^{II} has a square-planar co-ordination geometry with diamagnetism in chloroform solution. The signals of complexes containing Sm^{III} and Eu^{III} exhibited relatively small paramagnetic shifts and some signals showed coupling, but the signals of all the other complexes were shifted largely and broadened by the effects of the paramagnetic Ln^{III} as usually observed for lanthanoid(III) complexes. A broad signal at δ 4.6 was observed for Ni(edo)Lu_2, due to the hydrido protons bound to the boron atom. Assignments for the Ni(edo)Ln_2 series were made based on the integration ratios, 12 : 12 : 12 : 4 : 2. Three signals having integration of '12' are assigned to pyrazolyl protons and the others to oxamido protons, methylene (integration '4') and amido ('2') protons. The Ni(tdo)Ln_2 complexes have similar δ values for the pyrazolyl protons to those of the Ni(edo)Ln_2 complexes. With some exceptions, both series of pyrazolyl protons were observed in similar regions to those for [Ln{$HB(pz)_3$}$_2$L] type complexes.[19,20,28] The oxamido protons for the Ni(tdo)Ln_2 series give three signals, α-methylene ('4'), β-methylene ('2') and amido ('2') protons. The last two could not be assigned unambiguously, since they have the same integration ratios.

Measurements of the luminescence spectra in both dichloromethane solution (1×10^{-4} mol dm^{-3}) and in the solid state (powder) were attempted at room temperature for Ni(tdo)Eu_2, Ni(edo)Eu_2, Ni(tdo)Tb_2 and Ni(edo)Tb_2. However, no lanthanide-centred sharp emissions were detected. This may be due to the energy loss from the excited lanthanide(III) to the nickel(II) centre through the oxamido bridges.[4]

Table 2 Elemental analyses, IR and ^{1}H NMR spectra of the new complexes

		Elemental analysis (%)			IR/cm^{-1}		^{1}H NMR (δ)[b]				
							Pyrazolyl			Oxamido	
Complex	Yield[a] (%)	C	H	N	ν(B–H)	ν(C=O)				α-CH$_2$	β-CH$_2$ and/or NH
Ni(tdo)Eu$_2$	20	36.26 (36.19)	3.42 (3.40)	26.95 (27.49)	2457	1619	11.35	3.02	1.84	−3.68	−2.67 −6.23
Ni(tdo)Tb$_2$	22	36.20 (35.84)	3.40 (3.36)	26.90 (27.22)	2453	1622	30.0	5.4	−42.5		65.4 62
Ni(tdo)Yb$_2$	30	34.79 (35.15)	3.24 (3.29)	26.34 (26.70)	2454	1624	25.4	4.9	1.6	−18.4	−4.7 −22.5
Ni(edo)Sm$_2$	35	35.69 (35.78)	3.27 (3.30)	27.03 (27.82)	2453	1604 1633	8.72	6.03	4.11	1.58	4.07
Ni(edo)Eu$_2$	25	35.77 (35.70)	3.20 (3.29)	27.51 (27.76)	2456	1605 1633	11.63	3.00	1.65	1.60	−1.57
Ni(edo)Gd$_2$	34	35.80 (35.43)	3.35 (3.26)	27.51 (27.56)	2458	1607 1634					
Ni(edo)Tb$_2$	25	35.34 (35.35)	3.16 (3.26)	27.34 (27.49)	2457	1607 1636	32.5	4.5	−44.5	70.8	54
Ni(edo)Dy$_2$	35	35.09 (35.17)	3.30 (3.24)	26.80 (27.35)	2458	1608 1636	7.8	−14			−2.8
Ni(edo)Ho$_2$	35	34.63 (35.05)	3.25 (3.23)	26.59 (27.26)	2458	1608 1636	15.0	4.1	−36.5	29.4	57.8
Ni(edo)Er$_2$	37	35.42 (34.94)	3.31 (3.22)	26.60 (27.17)	2457	1609 1637	55.5	1.8	−12.3	−33.7	−24.3
Ni(edo)Tm$_2$	38	35.03 (34.86)	3.36 (3.21)	26.19 (27.11)	2459	1611 1639	4.6	−51.8		−47.0	−0.7
Ni(edo)Yb$_2$	29	34.83 (34.67)	3.17 (3.19)	26.82 (26.96)	2457	1612 1639	26.2	5.0	1.3	−19.0	−5.3
Ni(edo)Lu$_2$	34	34.74 (34.57)	3.13 (3.18)	26.59 (26.89)	2459	1613 1640	7.64	6.96	6.01	3.16	3.97

Calculated values are given in parentheses. [a] Repeated recrystallisations (six to eight times) of complexes of Eu$^{\text{III}}$ and Tb$^{\text{III}}$ sacrificed high yields (three times for the other complexes), since emission bands are observed due to small amounts of impurities. [b] Assignment based on the intergration ratios (see text). Owing to very large shifts and/or broadening, some signals are lacking.

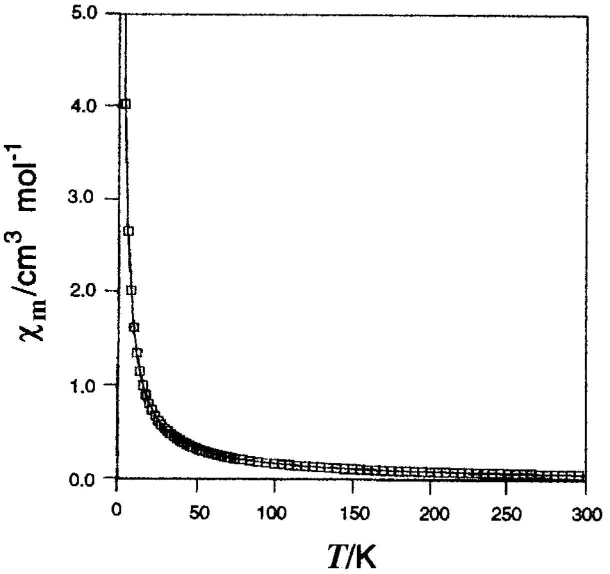

Fig. 1 Experimental temperature dependence of magnetic susceptibility for Ni(edo)Gd$_2$. The full line corresponds to the best data fit (see text)

Magnetic studies

The variable-temperature (2–300 K) magnetic susceptibility data collected for a microcrystalline sample of Ni(edo)Gd$_2$ are shown in Fig. 1. The nickel(II) ion is diamagnetic ($S_{\text{Ni}} = 0$) from the ^{1}H NMR spectrum of Ni(edo)Lu$_2$, and so Ni(edo)Gd$_2$ has two paramagnetic gadolinium(III) ions ($S_{\text{Gd}} = \frac{7}{2}$). The observed magnetic moment at room temperature is 11.38 μ_B which is somewhat larger than for two isolated gadolinium(III) ions (11.22 μ_B) ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}).

The magnitude of the spin-exchange interaction was estimated from susceptibility equations based on the Heisenberg spin-exchange operator $\boldsymbol{H} = -2J\cdot\boldsymbol{S}_1\cdot\boldsymbol{S}_2$. The molar susceptibility of a two gadolinium(III) ($S_{\text{Gd}} = \frac{7}{2}$) system is given by equation (1)

$$\chi_m = \{2Ng^2\beta^2[140 + 91\exp(14x) + 55\exp(26x) + 30\exp(36x) + 14\exp(44x) + 5\exp(50x) + \exp(54x)]\}/\{kT[15 + 13\exp(14x) + 11\exp(26x) + 9\exp(36x) + 7\exp(44x) + 5\exp(50x) + 3\exp(54x) + \exp(56x)]\} \quad (1)$$

where $x = -J/kT$, χ_m is the molecular susceptibility per trinuclear complex and the other symbols have their usual meanings. As shown in Fig. 1, a good fit to the experimental data is obtained for $J = -0.002$ cm^{-1} and $g = 2.03$. The agreement factor F, defined as $\Sigma[(\chi_m)_{\text{obs}} - (\chi_m)_{\text{calc}}]^2/\Sigma(\chi_m)_{\text{obs}}$, is then equal to 5×10^{-4}. This very small J is meaningless, so that there is no magnetic interaction between the two paramagnetic gadolinium(III) centres through the Ni(edo) moiety. This is in accordance with both that 4f electrons are shielded by the outer-shell electrons and that there is a large spacer Ni(edo) between the two Gd$^{\text{III}}$.

Crystallographic studies

Since dichloromethane–hexane solution was commonly used to crystallise most [Ln{HB(pz)$_3$}$_2$L] type complexes,[18–20,28] crystallisation of the new complexes for X-ray analysis was attempted in this solvent. However, the crystals obtained fractured upon removal from the mother-liquor and repeated attempts to mount them in capillaries containing the recrystallisation solvent failed to solve this problem. On the other hand, crystallisation from dichloromethane–acetonitrile solution afforded more robust and less efflorescent crystals of the new complexes so that the crystal structure analyses of both Ni(tdo)Yb$_2$ and

Table 3 Crystallographic data for Ni(tdo)Yb_2 and Ni(edo)Lu_2[a]

	Ni(tdo)Yb_2	Ni(edo)Lu_2
Formula	$C_{43}H_{48}B_4N_{28}NiO_4Yb_2\cdot 4CH_3CN$	$C_{42}H_{46}B_4Lu_2N_{28}NiO_4\cdot 2CH_3CN\cdot CH_2Cl_2$
M[b]	1633.27	1625.92
Space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	13.316(2)	11.513(2)
b/Å	15.823(2)	16.231(2)
c/Å	17.758(2)	18.082(2)
β/°	107.813(9)	98.72(1)
U/Å^3	3562.5(7)	3339.7(8)
D_c/Mg m^{-3}	1.522	1.618
μ(Mo-Kα)/mm^{-1}	2.929	3.357
F(000)	1620	1606
No. reflections measured	11 155	10 505
Transmission factors	0.509–1.000	0.833–1.000
No. reflections used[c]	5958	5047
No. parameters	385	397
R, R'	0.057, 0.084	0.074, 0.098

[a] Details in common: monoclinic; $Z = 2$; 296.2 K; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, $w^{-1} = \sigma_c^2(F_o) + (0.010|F_o|)^2$. [b] Solvated molecules included. [c] $I > 3\sigma(I)$.

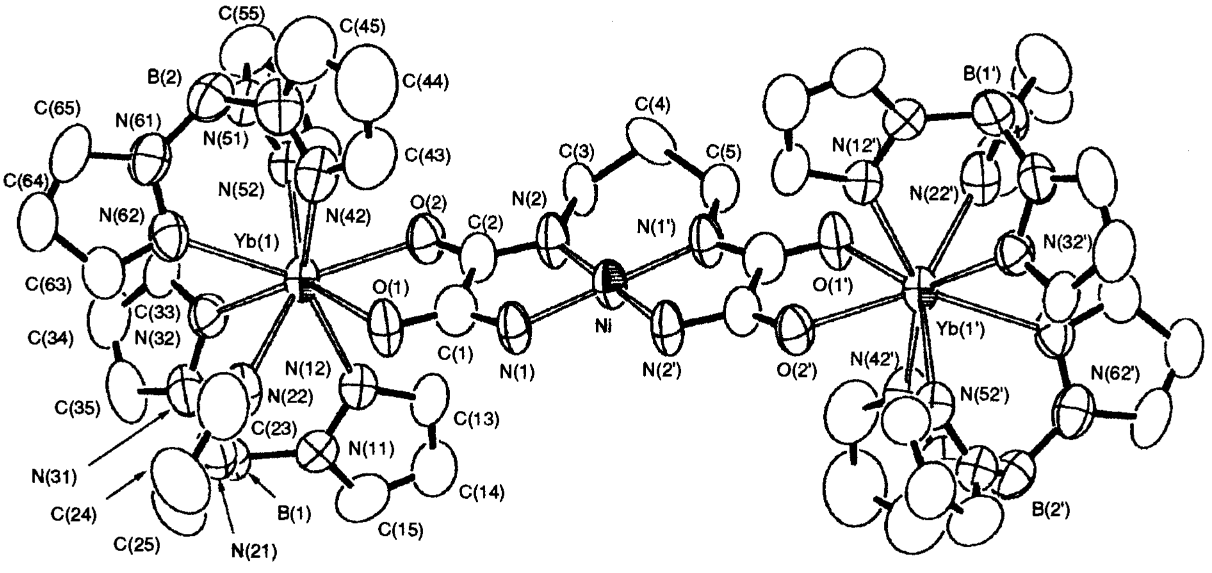

Fig. 2 Molecular structure of Ni(tdo)Yb_2 in the crystal, with the numbering scheme adopted

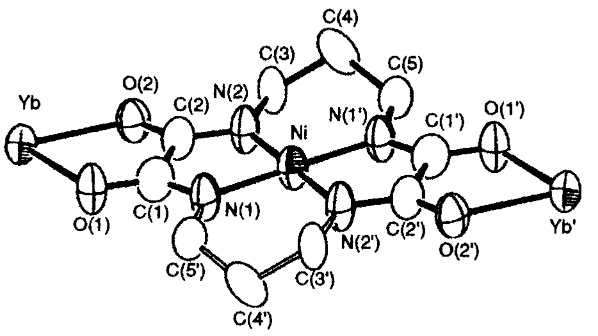

Fig. 3 An ORTEP[29] drawing showing only the Ni(tdo) moiety of Ni(tdo)Yb_2. The cyclic structure of the tdo ligand results from the orientational disorder of the trimethylene carbons [C(3), C(4) and C(5)]

Ni(edo)Lu_2 were performed by using this solvent. The elemental analyses of the samples before efflorescence indicated that four acetonitrile molecules per trinuclear complex Ni(tdo)Yb_2 and two acetonitrile and one dichloromethane molecule for Ni(edo)Lu_2 were included in the crystals. Crystal data, data collection parameters and results of the analysis are listed in Table 3, selected bond lengths and angles of Ni(tdo)Yb_2 and Ni(edo)Lu_2 in Tables 4 and 6, respectively.

Molecular structure of [Ni(tdo){Yb[HB(pz)$_3$]$_2$}$_2$]·4CH_3CN. The complex Ni(tdo)Yb_2 crystallises as efflorescent yellow monoclinic plates of space group $P2_1/n$. The molecular structure is illustrated in Fig. 2 which also shows the numbering scheme. Primed atoms are related to their unprimed equivalents by the inversion centre. The molecule seemingly has no inversion centre, but the Ni atom is located on a crystallographic centre of symmetry due to the orientational disorder (see Fig. 3 and later).

The Ni atom is located in a square-planar environment, with four oxamido nitrogens. The distances of Ni–N(1) and Ni–N(2) are similar, 1.904(9) and 1.902(8) Å, respectively. The Ni atom and the tdo ligand atoms [except C(4)] form a plane; the maximum deviation from this mean plane is 0.06 Å for C(5) and the deviation is only −0.018 Å for the Ni atom, but 0.098 Å for the Yb atom.

Each Yb atom is eight-co-ordinated with two tridentate HB(pz)$_3$ ligands and one didentate oxamide ligand Ni(tdo). The shortest ytterbium-to-ligand bond lengths are to the oxygen atoms, 2.296(8) and 2.309(7) Å for Yb–O(1) and Yb–O(2), respectively. The Yb–N bond lengths range from 2.36(1) to 2.485(9) Å, only two are very short, 2.36(1) and 2.385(9) Å for Yb–N(22) and Yb–N(52), respectively. The other four at *ca.* 2.47 Å are almost identical. The average Yb–N bond length is

2.44(2) Å, consistent with those found in related complexes containing $HB(pz)_3$ ligands, 2.478 Å for $[Yb\{HB(pz)_3\}_2(trop)]$ (Htrop = 2-hydroxycyclohepta-2,4,6-trien-1-one, tropolone),[19] 2.431 Å for $[Yb\{HB(pz)_3\}_2(O_2CPh)]$,[19] 2.486 Å for $[Yb\{HB(pz)_3\}_2(acac)]$[20] and 2.469 Å for $[Yb\{HB(pz)_3\}_3]$.[30] Each of the six pyrazole rings is almost planar; the deviation of any atom from the calculated least-squares plane is less than 0.03 Å. The distance Ni···Yb is 5.580 Å, compared to Cu···Gd in oxamate-bridged complexes $Gd_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$ (from 5.693 to 5.739 Å)[31] and Cu···Tm in $Tm_2[Cu(opba)]_3\cdot 10dmf\cdot 4H_2O$ (from 5.52 to 5.66 Å) [H_4pba = 1,3-propylenebis(oxamic acid), H_4opba = *ortho*-phenylenebis(oxamic acid)].[6]

The N_6O_2 co-ordination geometries [square antiprismatic (*SAPR*), bicapped trigonal prismatic (*TPRS*) and dodecahedral (*DD*)] were examined by using the semiquantitative method of polytopal analysis[32] and the values for δ and φ are presented in Table 5. From these values the most reasonable geometry around the Yb atom is a square antiprism. Fig. 4 shows a view of the donor atoms perpendicular to the square faces. Moss and Jones[19] reported that the co-ordination geometry around the Yb atom of $[Yb\{HB(pz)_3\}_2(trop)]$ is a square antiprism and that the δ values of O(2)[N(61)N(31)]N(41) and O(1)[N(11)N(51)]N(21) showing planarity of the 'squares' are 14.5 and 4.0°, respectively. In contrast, Ni(tdo)Yb_2 has δ values of 7.88 and 9.53°. These show that $[Yb\{HB(pz)_3\}_2(trop)]$ is on the geometric pathway to *TPRS* but that Ni(tdo)Yb_2 is to *DD*. The face formed by O(1), N(22),N(42) and N(62) is nearly planar (root-mean-square deviation of 0.071 Å), with the largest deviation from the least-squares plane being 0.084 Å for N(22). The O(2), N(12), N(32), N(52) face is less planar (root-mean-square deviation of 0.087 Å) with the largest deviation from the least-squares plane being 0.101 Å for N(32). The dihedral angle of these least-squares planes is 1.82°. The closest apices of the two squares consist of the two oxamido oxygen atoms; the O(1)···O(2) distance is 2.69(1) Å, which results from the relatively short Yb–O bond lengths and the small bite angle of O(1)–Yb–O(2). This is in contrast to the average N···N and O···N distances between the two squares of 3.00(2) and 3.09(1) Å, respectively.

Table 4 Selected bond lengths (Å) and angles (°) for Ni(tdo)Yb_2

Yb–O(1)	2.296(8)	O(1)–C(1)	1.26(1)
Yb–O(2)	2.309(7)	O(2)–C(2)	1.25(1)
Yb–N(12)	2.467(10)	N(1)–C(1)	1.30(1)
Yb–N(22)	2.36(1)	N(1)–C(5)	1.45(2)
Yb–N(32)	2.485(9)	N(2)–C(2)	1.32(1)
Yb–N(42)	2.47(1)	N(2)–C(3)	1.44(2)
Yb–N(52)	2.385(9)	C(1)–C(2)	1.55(2)
Yb–N(62)	2.484(9)	C(3)–C(4)	1.55(3)
Ni–N(1)	1.904(9)	C(4)–C(5)	1.49(3)
Ni–N(2)	1.902(8)		
O(1)–Yb–O(2)	71.6(2)	N(12)–Yb–N(22)	76.4(4)
O(1)–Yb–N(12)	81.0(3)	N(12)–Yb–N(32)	71.3(3)
O(1)–Yb–N(22)	72.9(3)	N(12)–Yb–N(42)	150.1(3)
O(1)–Yb–N(32)	143.8(3)	N(12)–Yb–N(52)	112.1(3)
O(1)–Yb–N(42)	75.2(3)	N(12)–Yb–N(62)	136.8(3)
O(1)–Yb–N(52)	137.7(3)	N(22)–Yb–N(32)	78.1(3)
O(1)–Yb–N(62)	119.9(3)	N(22)–Yb–N(42)	112.6(4)
O(2)–Yb–N(12)	75.1(3)	N(22)–Yb–N(52)	147.9(3)
O(2)–Yb–N(22)	137.2(3)	N(22)–Yb–N(62)	75.2(4)
O(2)–Yb–N(32)	120.8(3)	N(32)–Yb–N(42)	137.4(3)
O(2)–Yb–N(42)	80.3(3)	N(32)–Yb–N(52)	76.0(3)
O(2)–Yb–N(52)	73.5(3)	N(32)–Yb–N(62)	71.4(3)
O(2)–Yb–N(62)	144.7(3)	N(42)–Yb–N(52)	76.1(3)
N(1)–Ni–N(2)	85.7(4)	N(42)–Yb–N(62)	72.1(3)
N(1)–Ni–N(2′)	94.3(4)	N(52)–Yb–N(62)	78.8(3)
C(1)–N(1)–C(5)	118(1)	N(1)–C(1)–C(2)	113(1)
C(2)–N(2)–C(3)	118(1)	N(2)–C(2)–C(1)	112.9(9)
O(1)–C(1)–N(1)	129(1)	N(2)–C(3)–C(4)	113(1)
O(2)–C(2)–N(2)	128(1)	N(1)–C(5)–C(4)	114(1)
O(1)–C(1)–C(2)	116(1)	C(3)–C(4)–C(5)	113(2)
O(2)–C(2)–C(1)	118.0(10)		

A schematic drawing of Ni(tdo)Yb_2 is shown in Fig. 5(a). According to the definition of the absolute configuration (Λ and Δ) for the square antiprism as shown in Fig. 5(b), two Yb atoms in one molecule have opposite configurations, that is, Ni(tdo)Yb_2 has a *meso*-type structure. The strict molecular symmetry is C_1 but approximately C_s in which the Ni atom and the C(4) atom lie on the mirror plane, in view of the similarity in the bond lengths and angles around the Yb$\{HB(pz)_3\}$ and Ni(tdo) moieties as mentioned above.

Molecular structure of $[Ni(edo)\{Lu[HB(pz)_3]_2\}_2]\cdot 2CH_3CN\cdot CH_2Cl_2$. The complex Ni(edo)$Lu_2$ crystallises as efflorescent yellow monoclinic prismatic crystals of space group $P2_1/c$. The molecular structure is illustrated in Fig. 6 which also shows the numbering scheme in a similar fashion to that of Ni(tdo)Yb_2. However, the Ni atom is not located at an inversion centre (see Fig. 7 and next section).

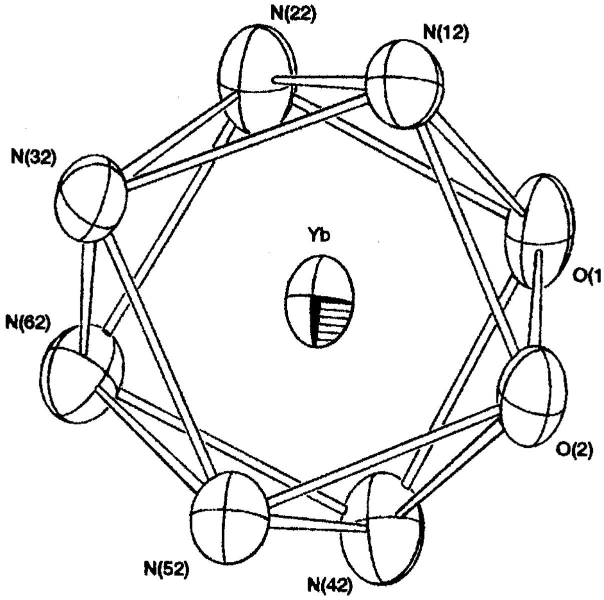

Fig. 4 An ORTEP drawing showing only the donor atoms co-ordinating to Yb. The view is perpendicular to one of the square faces of the square antiprism

Table 5 Values of δ and φ/° for Ni(tdo)Yb_2 and Ni(edo)Lu_2

			Idealised polyhedra		
Atoms	Ni(tdo)Yb_2	Ni(edo)Lu_2	*DD*	*SAPR*	*TPRS*
O(1)[N(22)N(42)]N(62)	δ 7.88	δ 8.47	29.5	0.0	21.8
O(2)[N(12)N(52)]N(32)	δ 9.53	δ 11.19	29.5	0.0	0.0
O(2)[N(42)N(52)]N(62)	δ 55.07	δ 55.06	29.5	52.5	48.2
O(1)[N(12)N(22)]N(32)	δ 54.03	δ 55.25	29.5	52.5	48.2
N(22)–O(1)–O(2)–N(52)	φ 24.21	φ 24.37	0.0	24.5	14.1
N(12)–N(32)–N(62)–N(42)	φ 21.92	φ 20.30	0.0	24.5	14.1

The Ni atom is located in a distorted square-planar environment with four oxamido nitrogens and an average Ni–N bond length of 1.82(7) Å. The average Lu–N bond length is 2.46(2) Å and Lu–O(1) and Lu–O(2) are 2.29(1) and 2.31(1) Å, respectively. The Ni • • • Lu distance is 5.59 Å. The Lu atoms are eight-co-ordinated and the most reasonable geometry of the co-ordination polyhedron is a distorted square antiprism as inferred from Table 5. The dihedral angle of the two squares O(1)–N(22)–N(42)–N(62) and O(2)–N(12)–N(32)–N(52) is 0.89°. These values and geometries around the lanthanide atom are very close to those of Ni(tdo)Yb_2.

Orientational and positional disorders. In Ni(tdo)Yb_2 the Ni atom is located on a crystallographic centre of symmetry. This result is consistent with the expected Z value of 2, but inconsistent with the molecular symmetry for the trinuclear complex predicted from the non-cyclic structure of the tdo ligand. Assuming orientational disorder for the trimethylene carbons of the tdo moiety [C(3), C(4) and C(5)] and populations of 0.5, the structure (Fig. 3) was expanded by subsequent Fourier syntheses. Fourier-difference synthesis indicated some electron densities for solvent molecules. Their geometrical features seemed to show two crystallographically independent acetonitrile molecules. This fact was consistent with the analytical result, but isotropic refinements for the atoms were unsuccessful. Thus, acetonitrile molecules with a relatively large thermal parameter ($B_{iso} = 10$ Å^2) were introduced at the most probable positions and fixed during the final refinement cycles. The crystal packing along the a axis including acetonitrile molecules is shown in Fig. 8. At both sides of the Ni(tdo) plane there are large spaces which allow a random occupation of the (loosely included) solvent molecules in the crystal.

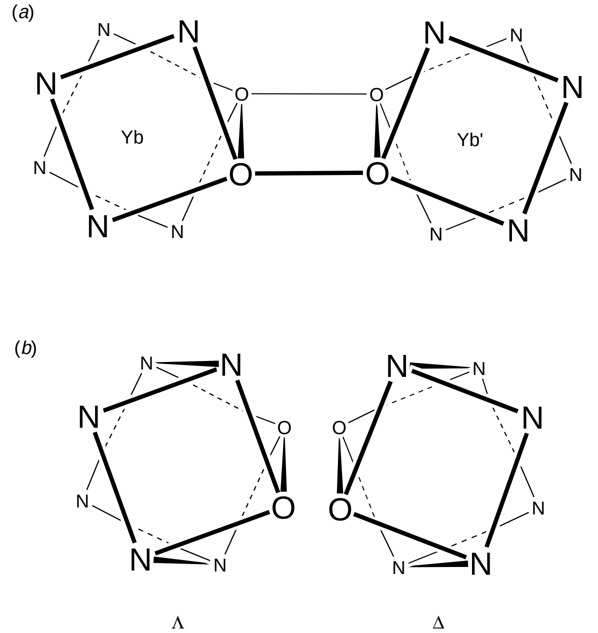

Fig. 5 (a) Schematic drawing of Ni(tdo)Yb_2 and (b) proposed definition of the absolute configuration (Λ and Δ) of the square antiprism

The structure of Ni(edo)Lu_2 was solved by a similar method to that of Ni(tdo)Yb_2, but the orientational disorder of the Ni(edo) moiety and the positional disorder of the solvated molecules gave more severe problems. Unlike Ni(tdo)Yb_2, the Ni atom is not located at a crystallographic centre of symmetry but very close to it. The severe disorder for the Ni(edo) moiety probably results from the fact that the bite angle of the five-membered edo ligand [N(2)–C(3)–C(4)–N(3)] is smaller than the six-membered tdo [N(2)–C(3)–C(4)–C(5)–N(1′)]. Thus, the N(2) • • • N(3) distance (2.43 Å) is quite shorter than N(1) • • • N(4) distance (2.98 Å) in Ni(edo)Lu_2 and N(1), N(2), N(3) and N(4) form a trapezoid, in contrast to a square plane for Ni(tdo)Yb_2. As a result, there are two sets of four positions for the edo nitrogen atoms (see Fig. 7). After the structural refinement of the trinuclear complex by a method similar to that for Ni(tdo)Yb_2, Fourier-difference synthesis suggested that some electron densities for solvated molecules were left. However, their geometries were featureless, albeit the elemental analyses suggested the existence of two acetonitrile and one dichloromethane molecules. Assuming completely random inclusion of the molecules in the crystals, the molecules were not introduced in the structural calculation.

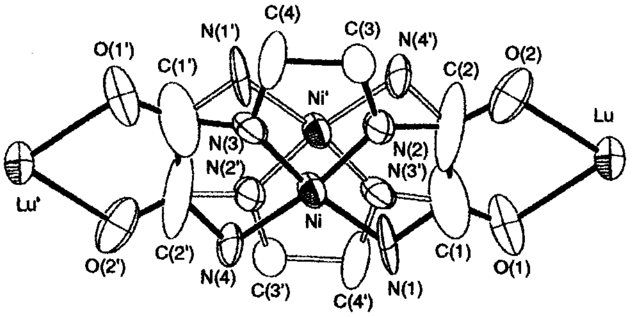

Fig. 7 An ORTEP drawing showing only the Ni(edo) moiety of Ni(edo)Lu_2. The oxamido nitrogens are in two sets of four positions due to the orientational disorder

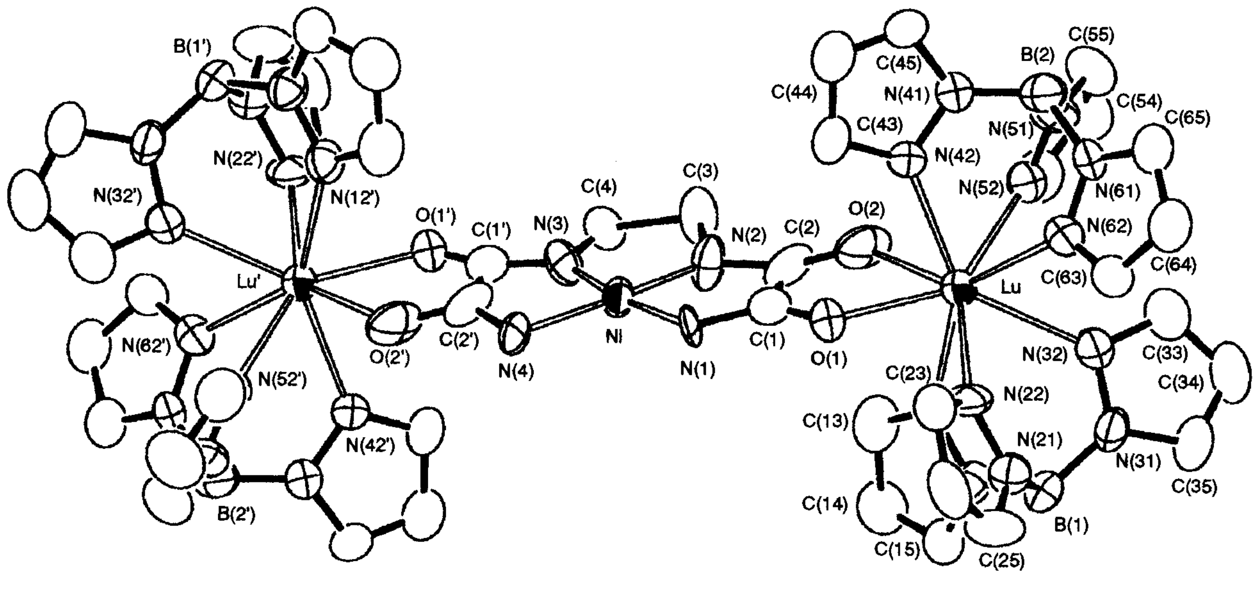

Fig. 6 Molecular structure of Ni(edo)Lu_2 in the crystal, with the numbering scheme adopted

Table 6 Selected bond lengths (Å) and angles (°) for Ni(edo)Lu_2

Lu–O(1)	2.29(1)	Ni–N(4)	1.89(3)
Lu–O(2)	2.31(1)	O(1)–C(1)	1.19(3)
Lu–N(12)	2.47(1)	O(2)–C(2)	1.28(3)
Lu–N(22)	2.40(1)	N(1)–C(1)	1.42(4)
Lu–N(32)	2.47(1)	N(2)–C(2)	1.35(3)
Lu–N(42)	2.50(1)	N(2)–C(3)	1.47(4)
Lu–N(52)	2.41(1)	N(3)–C(1′)	1.34(4)
Lu–N(62)	2.48(1)	N(3)–C(4)	1.43(6)
Ni–N(1)	1.85(5)	N(4)–C(2′)	1.46(4)
Ni–N(2)	1.78(3)	C(1)–C(2)	1.52(4)
Ni–N(3)	1.76(3)	C(3)–C(4)	1.62(5)
O(1)–Lu–O(2)	70.6(5)	N(2)–Ni–N(4)	170(1)
O(1)–Lu–N(12)	80.8(4)	N(3)–Ni–N(4)	84(1)
O(1)–Lu–N(22)	71.6(5)	N(12)–Lu–N(22)	75.7(4)
O(1)–Lu–N(32)	143.3(4)	N(12)–Lu–N(32)	71.4(4)
O(1)–Lu–N(42)	75.9(4)	N(12)–Lu–N(42)	149.7(4)
O(1)–Lu–N(52)	138.1(4)	N(12)–Lu–N(52)	112.0(5)
O(1)–Lu–N(62)	120.3(5)	N(12)–Lu–N(62)	139.1(4)
O(2)–Lu–N(12)	74.7(4)	N(22)–Lu–N(32)	78.6(4)
O(2)–Lu–N(22)	134.8(5)	N(22)–Lu–N(42)	113.9(4)
O(2)–Lu–N(32)	121.8(5)	N(22)–Lu–N(52)	149.0(4)
O(2)–Lu–N(42)	79.4(4)	N(22)–Lu–N(62)	78.9(4)
O(2)–Lu–N(52)	74.8(5)	N(32)–Lu–N(42)	137.4(4)
O(2)–Lu–N(62)	142.9(4)	N(32)–Lu–N(52)	76.1(4)
N(1)–Ni–N(2)	83(1)	N(32)–Lu–N(62)	72.6(4)
N(1)–Ni–N(3)	170(1)	N(42)–Lu–N(52)	75.3(4)
N(1)–Ni–N(4)	105(1)	N(42)–Lu–N(62)	70.6(4)
N(2)–Ni–N(3)	86(1)	N(52)–Lu–N(62)	76.8(4)
C(2)–N(2)–C(3)	109(3)	N(1)–C(1)–C(2)	125(3)
C(1′)–N(3)–C(4)	99(3)	N(3)–C(1′)–C(2′)	82(2)
O(1)–C(1)–N(1)	118(3)	N(2)–C(2)–C(1)	92(2)
O(2)–C(2)–N(2)	148(3)	N(4)–C(2′)–C(1′)	137(2)
O(1′)–C(1′)–N(3)	161(2)	N(2)–C(3)–C(4)	105(2)
O(2′)–C(2′)–N(4)	103(3)	N(3)–C(4)–C(3)	105(3)

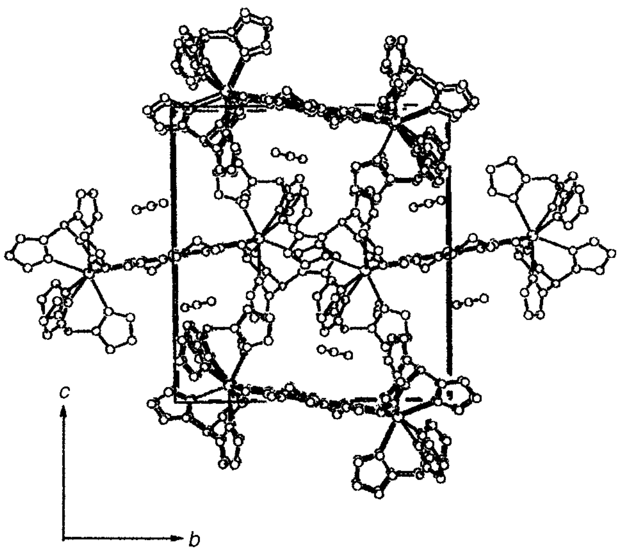

Fig. 8 Crystal packing along the *a* axis of Ni(tdo)Yb_2 including acetonitrile molecules

When the space group was reduced to the subgroups $P2_1$, $P\bar{1}$ and *Pn* (or *Pc*) the disorders of the Ni(tdo or edo) moiety and the solvated molecules could not be resolved. The present structure refinements have not yet given satisfactory solutions [$R = 0.057$ and 0.074 for Ni(tdo)Yb_2 and Ni(edo)Lu_2, respectively], probably owing to the random occupation of (loosely included) solvent. However, it is considered that the structures of the heterotrinuclear complexes with orientational disorder for the Ni(tdo or edo) moiety are basically correct and consistent with the elemental analyses and spectroscopic results.

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References

1 O. Kahn, *Struct. Bonding* (*Berlin*), 1987, **68**, 89.
2 G. Condorelli, I. Fragala, S. Giuffrida and A. Cassol, *Z. Anorg. Allg. Chem.*, 1975, **251**, 412.
3 Y. T. Li, D. Z. Liao, Z. H. Jiang and G. L. Wang, *Polyhedron*, 1995, **14**, 2209.
4 M. Sakamoto, Y. Kitakami, H. Sakiyama, Y. Nishida, Y. Fukuda, M. Sakai, Y. Sadaoka, A. Matsumoto and H. Okawa, *Polyhedron*, 1997, **16**, 3345 and refs. therein.
5 L. Chen, S. R. Breeze, R. J. Rousseau, S. Wang and L. K. Thompson, *Inorg. Chem.*, 1995, **34**, 454 and refs. therein.
6 R. L. Oushoorn, K. Boubekeur, P. Batail, O. Gillou and O. Kahn, *Bull. Soc. Chim. Fr.*, 1996, **133**, 777 and refs. therein.
7 J. L. Sanz, R. Ruiz, A. Gleizes, F. Lloret, J. Faus, M. Julve, J. J. Borras-Almenar and Y. Journaux, *Inorg. Chem.*, 1996, **35**, 7384 and refs. therein.
8 X. M. Chen, Y. L. Wu, Y. X. Tong and X. Y. Huang, *J. Chem. Soc., Dalton Trans.*, 1996, 2443 and refs. therein.
9 A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 485 and refs. therein.
10 I. Ramade, O. Kahn, Y. Jeannin and F. Robert, *Inorg. Chem.*, 1997, **36**, 930.
11 D. M. L. Goodgame, S. Menzer, A. T. Ross and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1994, 2605.
12 C. Piguet, G. Bernardinelli, J.-C. G. Bünzli, S. Petoud and G. Hopfgartner, *J. Chem. Soc., Chem. Commun.*, 1995, 2575.
13 S. J. Archibald, A. J. Blake, S. Parsons, M. Schröder and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 173.
14 Y. Yukawa, S. Igarashi, A. Yamano and S. Sato, *Chem. Commun.*, 1997, 711.
15 N. Sakagami, M. Tsunekawa, T. Konno and K. Okamoto, *Chem. Lett.*, 1997, 575.
16 C. Piguet, E. Rivara-Minten, G. Bernardinelli, J.-C. G. Bünzli and G. Hopfgartner, *J. Chem. Soc., Dalton Trans.*, 1997, 421.
17 E. K. Brechin, S. G. Harris, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1997, 1665.
18 M. A. J. Moss and C. J. Jones, *Polyhedron*, 1989, **8**, 117.
19 M. A. J. Moss and C. J. Jones, *J. Chem. Soc., Dalton Trans.*, 1990, 581.
20 M. A. J. Moss, C. J. Jones and A. J. Edwards, *J. Chem. Soc., Dalton Trans.*, 1989, 1393.
21 S. Trofimenko, *J. Am. Chem. Soc.*, 1967, **89**, 3170.
22 K. Nonoyama, H. Ojima and M. Nonoyama, *Inorg. Chim. Acta*, 1976, **20**, 127.
23 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
24 TEXSAN, Single Crystal Structure Analysis Software, version 1.7, Molecular Structure Corporation, The Woodlands, TX, 1995.
25 D. T. Cromer and J. T. Waber, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
26 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Determination, University of Göttingen, 1986.
27 Y. T. Li, Z. H. Jiang, D. Z. Liao, S. P. Yan, S. L. Ma, X. Y. Li and G. L. Wang, *Polyhedron*, 1993, **12**, 2781.
28 R. G. Lawrence, C. J. Jones and R. A. Kresinski, *J. Chem. Soc., Dalton Trans.*, 1996, 501.
29 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
30 M. V. R. Stainer and J. Takats, *Inorg. Chem.*, 1982, **21**, 4050.
31 O. Guillou, P. Bergerat, O. Kahn, E. Bakalbassis, K. Boubekeur, P. Batail and M. Guillot, *Inorg. Chem.*, 1992, **31**, 110.
32 M. G. B. Drew, *Coord. Chem. Rev.*, 1977, **24**, 179.

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