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Syntheses and specific structures of higher-order mixed chelate lanthanide complexes containing terpyridine, acetylacetonate, and nitrate ligands

Yutaka Fukuda,* Akiko Nakao and Katsura Hayashi

Department of Chemistry, Faculty of Science, Ochanomizu University, Otsuka, Bunkyo-ku, Tokyo, 112-8610, Japan. E-mail: fukuda@cc.ocha.ac.jp

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Novel higher-order mixed chelate complexes of lanthanide(III) have been synthesized, which contain 2,2′:6′,2-terpyridine (terpy, tridentate), 2,4-pentanedionate (acac, bidentate), and nitrate (NO_3^-, bidentate): general formula, [Ln(terpy)(acac)(NO_3)$_2$$H_2O_n$]. Thirteen quaternary chelating complexes of the lanthanide series (from La^{3+} to Lu^{3+} with the exception of Ce and Pm) have been obtained. In the series, complexes obtained using Nd(III) to Lu(III) (as the anhydrous compounds, $n = 0$) have a coordination number of nine and the lighter lanthanide (with larger ionic size) complexes contain one water molecule ($n = 1$, for La(III) coordination number, ten; and for Pr(III) coordination number, nine). The structural and characteristic properties of these complexes are as follows. (1) The five donor atoms (N_3O_2) from the ligands (terpy and acac) form a distorted pentagonal plane (equatorial) around the central lanthanide ion. (2) Except for the larger lanthanide complexes (La and Pr), two nitrate ligands are located at axial positions as bidentate ligands. (3) The ionic size effect of the central lanthanide ion reflects the variation in Ln–N(terpy) bond lengths. (4) The splitting parameter, $\Delta\nu$, of the NO_3^- ligand ($\nu_1 + \nu_4$ combination band which is observed at 1700–1800 cm^{-1} and splits into two weak components) increases with decreasing ionic size across the lanthanide series.

Introduction

Many studies on the synthesis of mixed ligand complexes have been reported to date, amongst which there are many examples of mixed chelate complexes with transition (d-block) metal ions such as Co(III), Pd(II) or Pt(II or IV). These central metal ions are relatively inert and undergo slow ligand exchange reactions.[1–3] On the other hand, for labile metal ion systems such as Cu(II) or Ni(II) complexes,[4–6] certain features such as electronic and/or steric factors should stabilize the mixed ligand complexes.[7] For example, we have synthesized many ternary complexes, *i.e.*, (1) mixed chelate complexes of Cu(II) containing β-diketonate (dike) and 2,2′-bipyridine (bipy), [Cu(dike)(bipy)]X,[8] and (2) Cu(II) and Ni(II) complexes of dike and the bulky *N*-alkylated ethylenediamine (diam), [M(dike)(diam)].[9] In these systems, one chelating ligand (bipy or diam) is rather bulky and exhibits interligand repulsion whilst its co-ligand is a less bulky chelating one such as dike or oxalate; the combination of these types of ligands results in the formation of stable mixed chelate complexes. Normally, however, these mixed chelate complexes are ternary systems owing to the small ionic sizes of the central (d-block) metals.

It is interesting and important to consider the degree of mixing of ligand components on the same metal ion, *i.e.*, ternary, quaternary, or quinquennary complexes as the mixed systems [M(A)(B)], [M(A)(B)(C)], [M(A)(B)(C)(D)], in order to understand the formation and structural consideration of any reaction intermediates. The aim of this work is to synthesize stable higher-order mixed chelate complexes containing labile metal ions such as lanthanide ions which have a relatively large ionic size. We have used 2,2′: 6′,2-terpyridine (terpy), which is a large, flat, π-acidic (π-back bonding) tridentate ligand,[10] acetylacetonate (acac),[11] and nitrate ion as the chelating ligands and examined the degree of mixing of the ligands. It is interesting to consider the structures of lanthanide complexes with higher coordination numbers. There are many reports on lanthanide ternary chelate complexes but few on higher-order mixed chelated systems. Thus far, for example, White and coworkers and others have reported the synthesis of some interesting ternary Ln complexes with terpy (or bipy or phen) and nitrate or carboxylate anions.[10] Among them, some quaternary systems have been reported with the system terpy–NO_3–H_2O, but there is no example of a quaternary chelating system as yet. In this study, we have obtained thirteen crystals of quaternary chelate complexes of the lanthanide series (from La^{3+} to Lu^{3+}, except Ce and Pm) and characterized the structural and IR spectroscopic properties of these complexes.

Experimental

Materials

The ligands (terpy and Hacac) and lanthanide nitrates used were obtained from Wako Chemicals, Co., Ltd., and Shin-etsu Kagaku Co., Ltd., respectively.

Syntheses of the mixed chelate complexes

The general method for synthesizing Ln(terpy)(acac)(NO_3)$_2$·nH_2O is as follows. To an ethanol solution of terpy, an equimolar amount of Ln(NO_3)$_3$·xH_2O ($x = 6$ for La, Pr–Dy, Er; $x = 5$ for Ho, Tm; $x = 4$ for Yb, Lu) in ethanol was added with vigorous stirring, resulting in the immediate formation of crystalline powders of Ln(terpy)(NO_3)$_3$·xH_2O for La–Gd, [Ln(terpy)(NO_3)$_2$(H_2O)$_3$]NO_3, for Tb–Lu, [Ln(terpy)(NO_3)$_2$(H_2O)$_2$](NO_3)$_2$·H_2O. To a solution of three molar amounts of acac (Hacac with NH_3 in ethanol), one molar amount of Ln(terpy)(NO_3)$_3$·xH_2O was added in solid form. This mixture was initially turbid, due to the suspended mixture of the ternary

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complex ($Ln(terpy)(NO_3)_3$ and acac ligand), but soon after, the solution became clear and then crystals of $Ln(terpy)(acac)(NO_3)_2 \cdot nH_2O$ appeared after a few days. Of these the La(III) and Pr(III) complexes have one water molecule ($n = 1$) and the other chelate compounds are anhydrous ($n = 0$). Analytical data and the color of the complexes obtained in this work are as follows (calculated values are shown in parentheses): $Ln(terpy)(acac)(NO_3)_2 \cdot H_2O$, Ln = La, colorless, C:38.57(39.16), H:3.21(3.28), N:11.94(11.42%); Ln = Pr, pale green, C:38.62(39.01), H:3.19(3.28), N:11.69(11.38%); $Ln(terpy)(acac)(NO_3)_2$, Ln = Nd, pale purple, C:40.16(39.99), H:2.89(3.02), N:11.59 (11.66%); Ln = Sm, pale yellow, C:39.80(39.59), H:2.91(2.99), N:11.46(11.54%); Ln = Eu, yellow, C:38.17(39.48), H:2.79(2.98), N:11.76(11.51%); Ln = Gd, colorless, C:39.08(39.16), H:2.76(2.95), N:11.64(11.41%); Ln = Tb, pale green, C:39.22 (39.04), H:2.91(2.95), N:11.35 (11.38%); Ln = Dy, colorless, C:38.82(38.81), H:2.81(2.93), N:11.10(11.32%); Ln = Ho, pale pink, C:38.66(38.66), H:2.96(2.96), N:11.12(11.27%); Ln = Er, pink, C:38.50(38.52), H:2.88(2.91), N:11.23(11.23%); Ln = Tm, colorless, C:38.43(38.41), H:2.86(2.90), N:10.99(11.20%); Ln = Yb, colorless, C:38.56(38.20), H:2.86(2.86), N:10.87(11.10%) and Ln = Lu, colorless, C:38.01(38.05), H:2.76(2.87), N:10.97(11.09%).

Crystal structure determination

Reflections from seven crystals {$[La(terpy)(acac)(NO_3)_2(H_2O)]$, $[Pr(terpy)(acac)(NO_3)_2(H_2O)]$, $[Nd(terpy)(acac)(NO_3)_2]$, $[Sm(terpy)(acac)(NO_3)_2]$, $[Gd(terpy)(acac)(NO_3)_2]$, $[Dy(terpy)(acac)(NO_3)_2]$ and $[Lu(terpy)(acac)(NO_3)_2]$} were collected at room temperature using the ω–2θ scan method on a Rigaku four-cycle system. Monochromatized Mo-Kα radiation was used ($\lambda = 0.71073$ Å). Lattice parameters were obtained from 24 reflections with $20 < 2\theta < 40°$. The data were corrected for Lorenz effects and absorption effects by the empirical Ψ-scan method. The data for the six remaining crystals {$[Eu(terpy)(acac)(NO_3)_2]$, $[Tb(terpy)(acac)(NO_3)_2]$, $[Ho(terpy)(acac)(NO_3)_2]$, $[Er(terpy)(acac)(NO_3)_2]$, $[Tm(terpy)(acac)(NO_3)_2]$ and $[Yb(terpy)(acac)(NO_3)_2]$} were collected with Mo-Kα radiation using the MacScience cylindrical Image Plate system. The crystals were positioned 120 mm from the image plate and 35 frames were measured at 6° intervals for 5 min at room temperature. Unit cell determination and indexing were performed using the DENZO program.[12] Absorption effects were corrected by integration based on the shape of the crystals. All data analyses were carried out with the maXus program.[13] The structures except for that of $[La(terpy)(acac)(NO_3)_2(H_2O)]$ were determined by direct methods with the SIR92[14] program and the structure of the La complex was determined using the SHLEXS-97 program.[15] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms that were not found by the difference Fourier method were included in idealized positions with fixed C–H distances, and isotropic thermal parameters were fixed to 1.2 times U_{eq} of the preceding carbon atom. All structures were refined on F^2 using the SHELXL97 program.[16] For the structure of $[La(terpy)(acac)(NO_3)_2(H_2O)]$, two nitrate ions were disordered over two orientations. The final structure was refined with occupancies of 58.3% and 41.7% for the two nitrate ions. Details of the crystallographic data are listed in Table 1. Significant bond distances and angles are shown in Table 2.

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See http://www.rsc.org/suppdata/dt/b1/b104468k/ for crystallographic data in CIF or other electronic format.

Physical measurements

Infrared (IR) spectra were recorded with a Perkin-Elmer FT-IR Spectrometer 2000 in KBr pellets in the 4000–370 cm^{-1} range at room temperature.

Results and discussion

Formation of mixed chelate complexes

We have obtained thirteen mixed chelate complexes of the lanthanide metal series from La(III) to Lu(III), with the exception of Ce(III) and Pm(III), which contain terpyridine (terpy), acetylacetonate (acac), and nitrate ions as the chelating ligands. For Ce(III), we could not obtain a solid sample as $Ce(terpy)(acac)(NO_3)_2$ or any other composition; this may be due to a redox reaction (the reaction solution became dark brown after mixing the metal ion and component ligands, and solid crystals could not be obtained). The general formula of the series obtained in this study is $Ln(terpy)(acac)(NO_3)_2 \cdot nH_2O$, where $n = 1$ for La^{3+} and Pr^{3+}, and the other eleven chelates (Nd^{3+}, Sm^{3+}–Lu^{3+}) are anhydrous crystals ($n = 0$). The elemental analyses of these complexes are shown in the Experimental section together with their colors, and the coordination numbers of the central metal ions determined by X-ray crystal structure analysis are ten for La^{3+} and nine for all of the other complexes. The lighter and larger lanthanide metal complexes (La(III) and Pr(III) mentioned above) have one coordinated water molecule forming quinquennary complexes, $[Ln(terpy)(acac)(NO_3)_2(H_2O)]$, of which the La(III) complex has a coordination number of ten and the Pr(III) complex of the same formula displays nine coordination, which indicates that one NO_3^- ion in the latter complex (Pr^{3+}) acts as a monodentate ligand (see structural discussion in the text). Moderately heavy lanthanide ions in this series have a coordination number of nine and contain three kinds of chelating ligands forming the quarternary system, $[Ln(terpy)(acac)(NO_3)_2]$ (from Nd(III) to Lu(III) except Pm).

It is noteworthy that the synthetic route to these mixed ligand complexes shown in the Experimental section is as follows (where the ternary chelate complexes, $Ln(terpy)(NO_3)_3 \cdot xH_2O$, are readily formed):

$$Ln(NO_3)_3 \cdot nH_2O \xrightarrow{terpy} Ln(terpy)(NO_3)_3 \cdot xH_2O \xrightarrow{3acac} [Ln(terpy)(acac)(NO_3)_2(H_2O)_n]$$

Thus, it is important to follow the exact sequence of mixing in order to obtain these higher-order mixed ligand complexes. If the process is changed, *i.e.*, when acac (3 molar amounts) was added first to the $La(NO_3)_3$ solution followed by terpy, only the $[Ln(acac)_3]$ chelates (with coordinated water molecule(s)) was obtained. Several attempts to obtain the ternary complexes $[Ln(terpy)(acac)_3]$ by the following routes (eqn. (1) and (2)) have been made:

$$Ln(acac)_3 + terpy(excess) \longrightarrow Ln(terpy)(acac)_3 \cdot xH_2O \qquad (1)$$

$$Ln(terpy)(NO_3)_3 \cdot xH_2O + acac(large\ excess) \longrightarrow Ln(terpy)(acac)(NO_3)_2 + NO_3^- \qquad (2)$$

However we have not succeeded in obtaining a ternary system containing terpy and acac ligands (eqn. (1)), $[Ln(terpy)(acac)_3]$ (see above, only the starting complex $[Ln(acac)_3]$, and the quaternary system have been observed (eqn. (2)). From the point of view of the coordination ability of the ligands, it is rather interesting to note that the ternary complexes $[Ln(terpy)(acac)_3]$ could not be formed directly from terpy and acac by the elimination of nitrate ligands (eqn. (2)), despite the observation that the acac ligand has a stronger chelating ability than NO_3.

When 2,2′-bipyridine (abbreviated as bipy) was used instead of terpy, $[Ln(bipy)(acac)_3(H_2O)_2]$[17] was easily obtained (see eqn. (3)) and also $[La(bipy)_2(NO_3)_3]$[18] (in both cases, the coordination number is ten).

$$Ln(acac)_3 + bipy \longrightarrow Ln(bipy)(acac)_3 \cdot 2H_2O \qquad (3)$$

Table 1 Crystal data of complexes

	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Formula	$LaC_{20}H_{20}N_5O_9$	$PrC_{20}H_{20}N_5O_9$	$NdC_{20}H_{18}N_5O_8$	$SmC_{20}H_{18}N_5O_8$	$EuC_{20}H_{18}N_5O_8$	$GdC_{20}H_{18}N_5O_8$	$TbC_{20}H_{18}N_5O_8$	$DyC_{20}H_{18}N_5O_8$	$HoC_{20}H_{18}N_5O_8$	$ErC_{20}H_{18}N_5O_8$	$TmC_{20}H_{18}N_5O_8$	$YbC_{20}H_{18}N_5O_8$	$LuC_{20}H_{18}N_5O_8$
Formula weight	613.31	615.31	600.63	606.79	608.35	613.64	615.32	615.32	621.32	623.65	629.43	629.43	631.36
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	15.74(3)	15.180(3)	11.037(3)	11.007(2)	10.994(3)	10.980(3)	10.975(1)	10.967(4)	10.945(2)	10.936(3)	10.922(2)	10.917(4)	8.967(4)
b/Å	7.938(9)	8.090(4)	14.373(3)	14.338(4)	14.328(3)	14.322(4)	14.295(2)	14.300(1)	14.291(4)	14.284(3)	14.278(4)	14.263(4)	28.2853(7)
c/Å	19.107(9)	18.892(3)	15.064(4)	15.032(2)	15.011(3)	15.001(3)	14.990(1)	14.975(2)	14.964(2)	14.935(3)	14.934(2)	14.915(5)	9.222(2)
β/°	99.97(8)	96.78(1)	102.34(2)	102.28(1)	102.28(2)	102.20(2)	102.233(9)	102.27(2)	102.27(1)	102.31(2)	102.25(1)	102.38(3)	106.33(2)
V/Å^3	2350.(5)	2304.0(10)	2335.0(10)	2318.1(8)	2310.8(10)	2305.8(9)	2298.3(4)	2294.9(8)	2287.2(7)	2279.0(10)	2275.8(8)	2269.0(10)	2245.0(10)
Space group	$P2_1/c$ (no.14)	$P2_1/c$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)
Z	4	4	4	4	4	4	4	4	4	4	4	4	4
μ/cm^{-1}	18.77	21.76	22.79	25.88	27.70	29.39	31.33	33.12	35.19	37.38	39.54	41.79	44.55
T/K	298	298	298	298	298	298	298	298	298	298	298	298	298
No. of independent reflections	5398	5291	5363	5123	5239	5519	5205	5172	5172	4985	5133	3981	5152
R_{int}	0.013	0.004	0.021	0.023	0.027	0.036	0.025	0.015	0.040	0.024	0.031	0.043	0.043
R all; R^a	0.0836; 0.0337	0.0777; 0.0403	0.0786; 0.0358	0.0724; 0.0553	0.0445; 0.0343	0.0455; 0.0333	0.0396; 0.0305	0.0853; 0.0401	0.0427; 0.0353	0.0428; 0.0359	0.0411; 0.0315	0.1272; 0.0685	0.0710; 0.0355
R_w all; $R_w{}^b$	0.1084; 0.0773	0.0978; 0.0834	0.0985; 0.0746	0.1300; 0.0880	0.0926; 0.0830	0.1000; 0.1000	0.0740; 0.0679	0.1164; 0.0887	0.0966; 0.0907	0.0983; 0.0908	0.0837; 0.0745	0.2770; 0.1925	0.0989; 0.0813

[a] $R = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$ [b] $wR = \{\Sigma w|F_o^2| - |F_c^2|\}^2/\Sigma w|F_o^2|^2\}^{1/2}$, $w = 1/(\sigma^2(F_o^2) + (AP)^2 + BP)$ where $P = (F_o^2 + 2F_c^2)/3$

Table 2 Selected bond lengths (Å) and angles (°)

Ln	La	Pr	Nd	Sm	Eu	Gd	Tb
Ln(1)–O(1)	2.413(5)	2.346(3)	2.346(4)	2.315(8)	2.314(3)	2.31(1)	2.290(3)
Ln(1)–O(2)	2.430(5)	2.415(4)	2.330(4)	2.311(7)	2.289(3)	2.283(10)	2.261(3)
Ln(1)–O(3)	2.703(2)	2.671(4)	2.539(4)	2.512(8)	2.506(4)	2.49(1)	2.474(3)
Ln(1)–O(4)	2.622(12)	2.615(4)	2.567(4)	2.546(8)	2.523(3)	2.533(10)	2.508(3)
Ln(1)–O(6)	2.720(10)	3.17(1)	2.521(4)	2.482(8)	2.474(4)	2.46(1)	2.445(3)
Ln(1)–O(7)	2.707(10)	2.581(5)	2.557(4)	2.539(8)	2.524(3)	2.52(1)	2.506(3)
Ln(1)–O(9)	2.560(5)	2.518(4)					
Ln(1)–N(1)	2.688(7)	2.604(4)	2.620(5)	2.590(8)	2.585(4)	2.58(1)	2.564(3)
Ln(1)–N(2)	2.730(5)	2.678(4)	2.611(4)	2.569(8)	2.559(4)	2.56(1)	2.530(3)
Ln(1)–N(3)	2.680(5)	2.618(4)	2.597(4)	2.566(9)	2.555(3)	2.57(1)	2.537(3)
O(1)–C(17)	1.287(7)	1.274(6)	1.254(7)	1.244(12)	1.259(5)	1.27(2)	1.265(5)
O(2)–C(19)	1.265(7)	1.277(6)	1.275(7)	1.273(13)	1.275(6)	1.27(2)	1.277(5)
O(3)–N(4)	1.19(2)	1.253(6)	1.262(6)	1.250(11)	1.270(6)	1.24(2)	1.263(5)
O(4)–N(4)	1.428(18)	1.260(6)	1.256(7)	1.263(11)	1.258(6)	1.25(2)	1.259(5)
O(5)–N(4)	1.227(7)	1.215(6)	1.211(7)	1.211(12)	1.210(6)	1.23(1)	1.209(5)
O(6)–N(5)	1.237(14)	1.210(6)	1.273(7)	1.287(12)	1.267(6)	1.25(2)	1.273(5)
O(7)–N(5)	1.250(16)	1.232(7)	1.260(7)	1.235(12)	1.264(6)	1.26(2)	1.260(5)
O(8)–N(5)	1.200(7)	1.201(6)	1.211(7)	1.223(12)	1.210(6)	1.20(2)	1.213(5)
C(16)–C(17)	1.505(9)	1.493(7)	1.492(9)	1.523(15)	1.500(7)	1.498(16)	1.502(6)
C(17)–C(18)	1.375(10)	1.391(8)	1.399(9)	1.382(16)	1.401(7)	1.38(2)	1.401(6)
C(18)–C(19)	1.383(10)	1.385(8)	1.390(9)	1.389(16)	1.381(7)	1.38(2)	1.384(6)
C(19)–C(20)	1.501(9)	1.511(8)	1.505(8)	1.480(15)	1.506(7)	1.495(15)	1.499(6)
O(1)–Ln(1)–O(2)	71.71(16)	72.75(13)	73.57(14)	74.6(3)	74.82(11)	75.6(4)	75.55(10)
O(3)–Ln(1)–O(4)	47.5(4)	47.72(12)	49.67(15)	50.0(3)	50.65(12)	49.7(3)	50.86(11)
O(6)–Ln(1)–O(7)	45.33(18)	41.1(3)	50.14(15)	50.8(3)	50.92(12)	50.4(4)	51.56(11)
N(1)–Ln(1)–N(2)	59.87(18)	61.83(14)	62.42(15)	62.6(3)	63.48(12)	64.5(5)	63.92(11)
N(2)–Ln(1)–N(3)	60.10(18)	61.47(14)	62.47(15)	63.7(3)	63.75(11)	63.3(4)	64.58(10)
O(3)–N(4)–O(4)	115.5(10)	116.7(5)	116.8(5)	116.5(10)	116.6(4)	115(1)	116.1(3)
O(6)–N(5)–O(7)	115.9(9)	117.7(7)	116.3(5)	117.3(10)	116.2(4)	115(1)	116.5(3)
O(1)–C(17)–C(18)	124.0(6)	124.0(5)	125.1(6)	125.6(11)	124.8(4)	124.8(12)	124.3(4)
C(17)–C(18)–C(19)	127.0(6)	126.4(5)	125.4(6)	126.8(11)	125.3(4)	124.4(12)	125.7(4)
C(18)–C(19)–O(2)	125.3(6)	125.2(5)	124.1(6)	122.5(11)	124.7(4)	126.3(11)	124.0(4)

Ln	Dy	Ho	Er	Tm	Yb	Lu
Ln(1)–O(1)	2.278(5)	2.276(7)	2.259(3)	2.250(3)	2.238(14)	2.233(4)
Ln(1)–O(2)	2.249(5)	2.256(7)	2.226(3)	2.222(3)	2.211(12)	2.207(4)
Ln(1)–O(3)	2.467(6)	2.452(8)	2.435(4)	2.426(4)	2.552(15)	2.412(5)
Ln(1)–O(4)	2.505(5)	2.513(8)	2.482(4)	2.477(3)	2.458(13)	2.450(5)
Ln(1)–O(6)	2.431(6)	2.430(8)	2.402(4)	2.391(4)	2.519(13)	2.360(4)
Ln(1)–O(7)	2.515(6)	2.514(8)	2.484(4)	2.480(4)	2.478(14)	2.478(5)
Ln(1)–O(9)						
Ln(1)–N(1)	2.569(6)	2.560(8)	2.531(4)	2.525(4)	2.523(17)	2.469(5)
Ln(1)–N(2)	2.513(6)	2.504(8)	2.477(4)	2.468(4)	2.475(16)	2.469(5)
Ln(1)–N(3)	2.517(6)	2.524(9)	2.501(4)	2.485(4)	2.451(15)	2.504(5)
O(1)–C(17)	1.268(9)	1.27(1)	1.271(6)	1.267(6)	1.31(3)	1.289(8)
O(2)–C(19)	1.283(9)	1.27(1)	1.270(7)	1.268(6)	1.33(3)	1.267(8)
O(3)–N(4)	1.273(8)	1.28(1)	1.264(6)	1.265(6)	1.14(2)	1.272(7)
O(4)–N(4)	1.261(9)	1.28(1)	1.254(6)	1.250(6)	1.28(3)	1.252(7)
O(5)–N(4)	1.206(9)	1.21(1)	1.211(7)	1.212(6)	1.26(3)	1.219(7)
O(6)–N(5)	1.274(9)	1.29(2)	1.272(6)	1.269(6)	1.15(2)	1.278(7)
O(7)–N(5)	1.248(9)	1.25(2)	1.261(6)	1.252(6)	1.38(2)	1.252(8)
O(8)–N(5)	1.215(9)	1.23(1)	1.212(6)	1.215(6)	1.25(2)	1.222(8)
C(16)–C(17)	1.492(11)	1.495(7)	1.500(8)	1.502(6)	1.507(8)	1.497(10)
C(17)–C(18)	1.413(11)	1.39(2)	1.394(7)	1.393(7)	1.39(3)	1.389(9)
C(18)–C(19)	1.378(11)	1.38(2)	1.386(8)	1.382(7)	1.32(3)	1.382(9)
C(19)–C(20)	1.503(11)	1.499(7)	1.499(8)	1.499(6)	1.501(8)	1.502(9)
O(1)–Ln(1)–O(2)	75.92(19)	76.4(3)	76.62(13)	76.77(12)	77.0(5)	78.24(16)
O(3)–Ln(1)–O(4)	51.27(19)	51.9(3)	51.42(13)	51.54(12)	50.4(5)	52.15(16)
O(6)–Ln(1)–O(7)	51.6(2)	52.2(3)	52.16(13)	52.26(13)	52.3(5)	52.54(17)
N(1)–Ln(1)–N(2)	64.8(2)	64.2(3)	64.70(13)	64.93(13)	64.6(6)	66.20(18)
N(2)–Ln(1)–N(3)	64.67(19)	65.5(3)	65.32(13)	65.69(12)	65.8(5)	64.92(17)
O(3)–N(4)–O(4)	116.3(7)	115(1)	115.9(4)	116.0(4)	123.1(16)	115.8(5)
O(6)–N(5)–O(7)	117.3(7)	117(1)	116.1(4)	116.8(4)	121.2(15)	115.8(6)
O(1)–C(17)–C(18)	123.5(7)	124.3(4)	124.8(5)	124.3(4)	124.9(5)	124.8(6)
C(17)–C(18)–C(19)	126.0(7)	125.4(4)	125.1(5)	125.7(4)	124.5(5)	125.2(6)
C(18)–C(19)–O(2)	123.9(7)	124.5(5)	124.2(5)	124.0(4)	124.3(5)	124.9(6)

The key ligand that forms a higher-order (quaternary) complex is terpy which is a rigid planar ligand. If terpy and one acac ligand form a pentagonal plane (equatorial) similar to the case of the quaternary system obtained in this work (see the crystal structures of this series), there is insufficient space for the remaining two acac ligands to coordinate in the axial positions and form the ternary system, [Ln(terpy)(acac)$_3$]. In the case of the NO$_3^-$ bidentate ligand which has a rather small bite angle with respect to that of the Ln^{3+} ion, we could readily obtain the ternary system, $Ln(terpy)(NO_3)_3 \cdot xH_2O$. Consequently, in this work, the combination of terpy, one acac and two NO_3^- chelating ligands is suitable for formimg nine coordinated metal ions with a quaternary system around the central Ln^{3+} ion.

Structure and bonding in mixed chelate complexes

Thirteen single crystals of these complexes have been obtained, and their structures determined by X-ray diffraction.

These crystal structures are classified into three categories, (1) those with a coordination number of ten with three chelating ligands (terpy is tridentate; acac and two NO_3 ligands are all bidentate) and one water molecule: $La(terpy)(acac)(NO_3)_2 \cdot H_2O$, (2) those with a coordination number of nine with a composition similar to that of the La^{3+} complex described above: $Pr(terpy)(acac)(NO_3)_2 \cdot H_2O$, in which the coordination mode of the two nitrates is different, one is monodentate and another bidentate, and (3) those with a coordination number of nine without any water molecule (from Nd to Lu). Some of these crystal structures are shown in Figs. 1–3: category (1) is represented by La(III) in Fig. 1, category (2) by Pr(III) in Fig. 2, and category (3) by Tb(III) in Fig. 3.

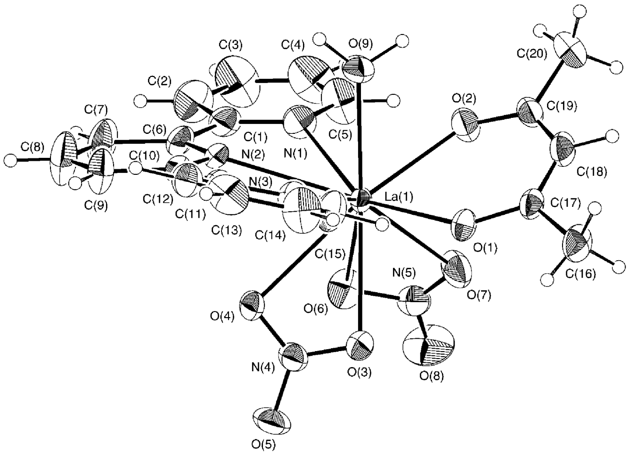

Fig. 1 ORTEP[19] diagram of $[La(terpy)(acac)(NO_3)_2(H_2O)]$.

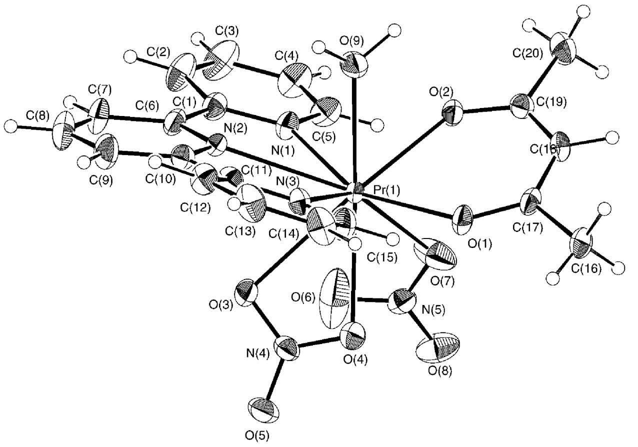

Fig. 2 ORTEP diagram of $[Pr(terpy)(acac)(NO_3)_2(H_2O)]$.

The lighter lanthanides (La(III) and Pr(III)) have ionic radii larger than those of the heavier lanthanide ions and although they both contain one water molecule as a monodentate ligand, the coordination geometries of the two compounds are different from each other, *i.e.*, the La(III) complex has completel coordination of the chelating ligands, terpy, acac and NO_3^- and one water molecule resulting in 10-coordination (Fig. 1). The ligands terpy and acac can form a distorted pentagonal plane with two NO_3^- ligands located below and a water molecule above the plane in the complex (see Fig. 1). The Pr(III) complex has 9-coordination in which the position of the ligands around the central Pr metal ion is nearly the same as that in the case of La(III) mentioned above; however one NO_3^- ligand acts in a monodentate fashion (see Fig. 2). From the crystal data of the Pr(III) complex, the NO_3^- acting as a monodentate ligand has a rather short bond distance (Pr–O7 2.581(5) Å), with the Pr–O6 distance being rather long (3.17(1) Å); the bond angles are Pr–O7–N 114.1(5)° and Pr–O6–N 84.4(6)°. Therefore, we conclude that the coordination mode of this NO_3^- is monodentate. In the case of the complexes containing a coordinated water molecule (La^{3+} and Pr^{3+}), there is hydrogen bond formation between the coordinated water molecule and the neighboring nitrate ligand.

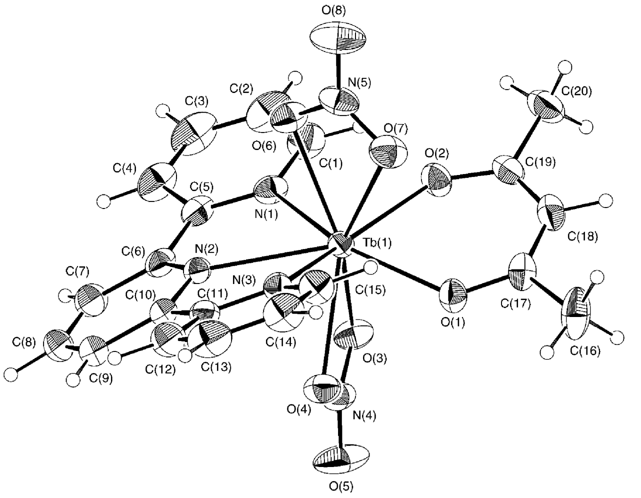

Fig. 3 ORTEP diagram of $[Tb(terpy)(acac)(NO_3)_2]$.

We next discuss the anhydrous quarternary lanthanide complexes in the series. The Nd(III) complex, $[Nd(terpy)(acac)(NO_3)_2]$, has 9-coordination in which terpy and acac are near the same pentagonal plane (equatorial) and two bidentate NO_3^- ligands are located above and below the equatorial (distorted pentagonal) plane formed by terpy and acac (see Fig. 3). Other heavier lanthanide complexes (Sm–Lu) are also anhydrous and have the same structure as that of the Tb(III) complex (9-coordination) shown in Fig. 3. Among them, crystal packing in the Lu(III) complex is different from the other anhydrous complexes, although the space group of Ln(III) is the same (isomorphous) as that of the other anhydrous complexes.

Based on the results obtained in this study, we can conclude that the crystals contain three types of ligand, *i.e.*, one tridentate (terpy) and two bidentate (acac and nitrate) ligands among which the positions of the terpyridine and acetylacetonate ligands are uniquely oriented to form an equatorial pentagonal distorted plane; there are no exceptions across this series. As mentioned by White and co-workers,[10] there are similar hydrogen bond interactions between the '*ortho*'-hydrogens (6 and 6″ hydrogens, in our numbering system H1 and H15 hyrogens in Fig. 3) of terpy and two oxygen donors of acac in this series (estimated O ··· H bond lengths, 2.334 and 2.878 Å, respectively, in the Tb-complex).

It is noteworthy, as already discussed in the Introduction, that the mixed ligand complexes of Cu(II) containing bipy and pyrocatecholate (or β-diketonate) can be formed with much higher stability due to the π-acid and π-base interligand interaction (electronic effect). In this case, the combination of terpy and acac in the same plane may have occured due to the similar types of interactions. This electronic and steric basis for compound formation reflects the easy formation of a higher-order mixed chelate system (not ternary but quaternary), Ln–terpy–acac–NO_3.

The next interesting point is the length of the bonds between the central lanthanide ion and the donor atom in the series. Fig. 4 shows Ln–O(acac or NO_3) bond length variations (for

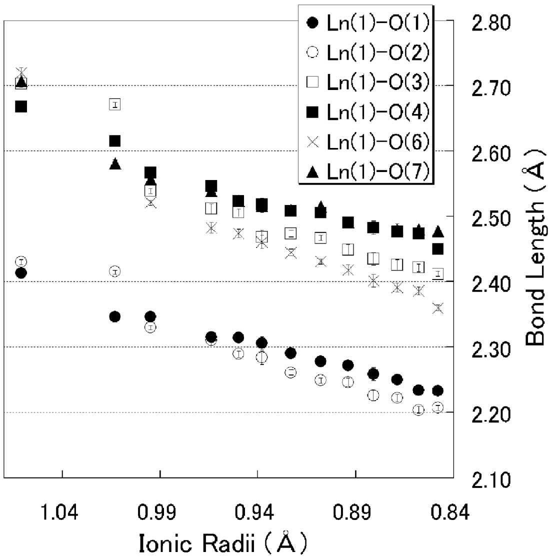

Fig. 4 Ln–O bond length *vs.* ionic size for the central Ln(III) ions.

the numbering of the donor atoms, see Fig. 3 as an example). From these data, we can conclude that (1) in both Ln–O(acac and nitrate) bonds, the bond length decreases with a decrease in ionic size, and (2) Ln–O(acac) bond lengths are shorter than those of the analogous Ln–O(NO_3) ones.

The relationship between the three Ln–N(terpy) bond lengths and the central metal ion size shows (1) a similar trend to that mentioned above (in Fig. 4) for the Ln–O bond length variation and (2) the variation of these three bond lengths in the respective complexes. In the larger lanthanide complexes, the Ln–N2 bond (dotted line in Fig. 5, lower part) is the longest of the three Ln–N(terpy) bonds. This is explained by the lanthanide ionic size and the rigid and planar coordination of the three nitrogen donors of terpyridine, which is shown in Fig. 5 as a relationship between the ionic size of the central metal and the Ln–N bond lengths. Larger lanthanide ions can form coordinate bonds with the terpy ligand in which the central N2 donor atom is located at a further position from the lanthanide ion than in the case of the N1 or N3 donors (upper part in Fig. 5). On the other hand, in the case of the heavier lanthanide ions of the series (Ln^{3+} with smaller ionic size), the longest Ln–N bond is observed either at the Ln–N1 or Ln–N3 (terminal N-donor).

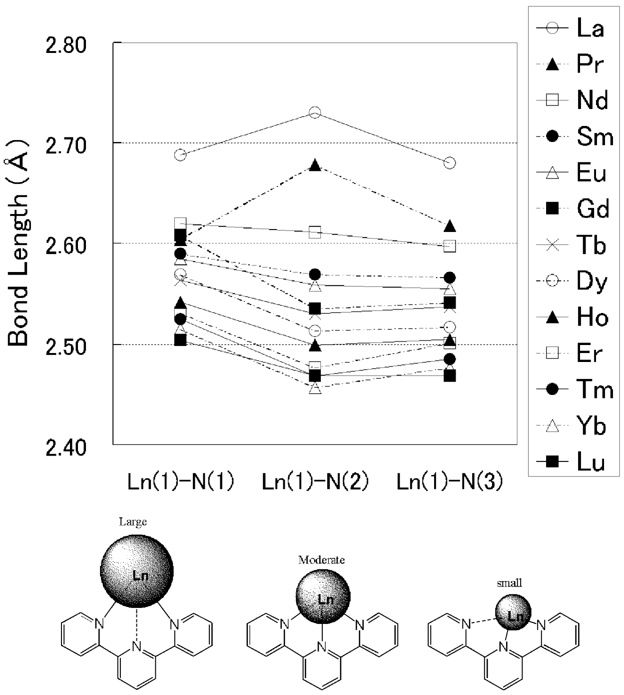

Fig. 5 The planar chelate structure of terpy and the relationship between lanthanide ionic size and Ln–N bond length (where N(1) and N(3) are terminal nitrogen donors and N(2) is a central donor on terpy).

Table 3 Characteristic IR peaks and $\Delta\nu$ values

Ln	acac $\nu_{C=O} + \nu_{C=C}$	NO_3 $\nu_1 + \nu_4$	$\Delta\nu$
La	1574.58, 1520.12	1772.98, 1743.13	29.85
Pr	1598.81, 1524.81	1772.52, 1744.14	28.38
Nd	1597.68, 1519.68	1764.40, 1732.72	31.68
Sm	1596.04, 1519.54	1767.88, 1733.55	34.33
Eu	1574.72, 1520.00	1769.94, 1733.30	36.64
Gd	1597.08, 1519.42	1771.76, 1734.53	37.23
Tb	1597.76, 1519.82	1773.58, 1735.58	38.00
Dy	1598.60, 1518.96	1772.07, 1734.22	37.85
Ho	1598.74, 1520.05	1774.26, 1735.82	38.44
Er	1574.52, 1520.10	1777.65, 1736.63	41.02
Tm	1599.49, 1520.31	1779.25, 1737.90	41.35
Yb	1599.50, 1521.11	1781.58, 1738.56	42.55
Lu	1599.92, 1520.86	1781.58, 1738.56	43.02

Finally, it is noteworthy that there is a relationship between the lanthanide contraction and the volume of the complexes, which means that the volume of the unit cells of the complexes decreases with an increase in the atomic number of the lanthanide ion (see Table 1).

IR spectra and the ionic size of the lanthanide metal ions

In Fig. 6, as an example, an IR spectrum of [Sm(terpy)(acac)(NO_3)$_2$] is shown, in which there are two strong bands at 1595 and 1516 cm^{-1} due to $\nu_{C=O}$ and $\nu_{C=C}$ of acetylacetonate.[20] In this spectrum, it is noteworthy that the combination band (ν_1 + ν_4) of the NO_3^- ligand appears to split into two weak bands in the region 1800–1700 cm^{-1} in addition to the broad band around 1300–1500 cm^{-1}. The width of the splitting parameter in cm^{-1} ($\Delta\nu$) obtained from these weak bands is a good criterion for ascertaining the coordination mode of NO_3^- to the central metal ion, *i.e.*, the splitting for bidentate coordination is more than 25 cm^{-1}, for monodentate less than approximately 25 cm^{-1}, and there is no splitting for ionic (not coordinated) bonds. In Table 3,[21] characteristic IR bands of acac and those of the NO_3^- bands are shown with the splitting parameters ($\Delta\nu$). The plots of $\Delta\nu$ *vs.* atomic number for a series of lanthanides are shown in Fig. 7.

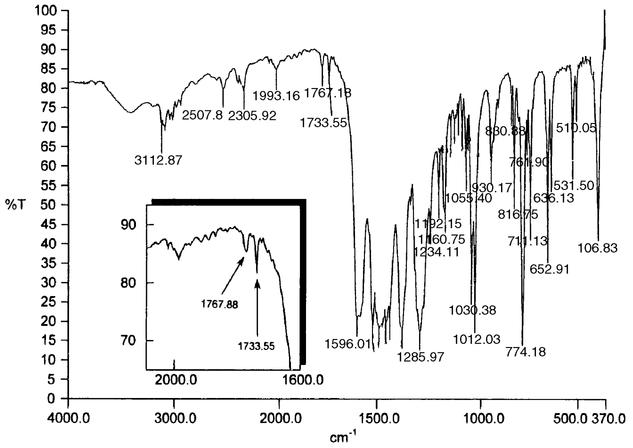

Fig. 6 IR spectra of Sm(terpy)(acac)(NO_3)$_2$.

From these data, $\Delta\nu$ values are rather large which shows the bidentate coordination mode of the NO_3 ligand. The plots of

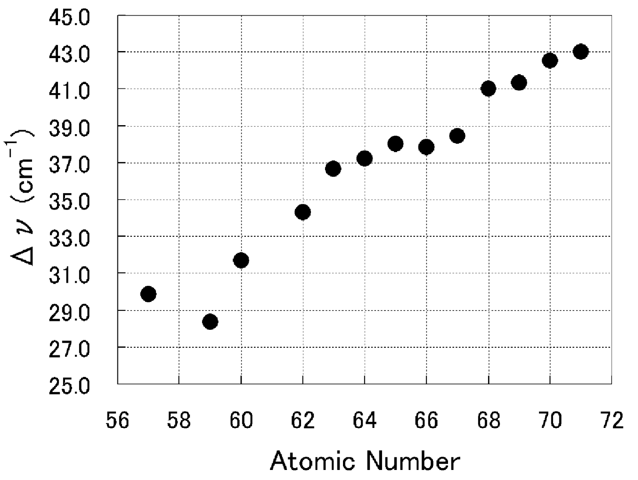

Fig. 7 Plot of $\Delta\nu$ values of NO_3^- *vs.* atomic number for the Ln series

$\Delta\nu$ *vs.* atomic number of the lanthanide series indicate a rather good linear relationship, among which the smaller lanthanide complexes have larger splitting values of $\Delta\nu$. In other words, the smaller the ionic size of the central metal ion, the stronger is the interaction of the lanthanide metal ion with NO_3^-.

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References

1 (*a*) T. Fujiwara, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 122; (*b*) G. Grassini-Strazza, M. Sinibaldi and A. Messiaa, *Inorg. Chim. Acta*, 1980, **44**, L295.

2 Y. Kobayashi, N. Nagao, S. Okeya and Y. Fukuda, *Chem. Lett.*, 1996, 663.

3 *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vols. 3–5 and references therein.

4 H. Sigel and D. B. McCormick, *Acc. Chem. Res.*, 1970, **3**, 201.

5 G. A. L. Heureux and A. E. Martell, *J. Inorg. Nucl. Chem.*, 1966, **28**, 481.

6 Y. Fukuda and K. Sone, *J. Inorg. Nucl. Chem.*, 1972, **34**, 2315.

7 Y. Yamada, T. Hoshi and Y. Fukuda, *J. Coord Chem.*, 1996, **38**, 1.

8 Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 556.

9 K. Sone and Y. Fukuda, *Inorganic Thermochromism*, Springer, Heidelberg, 1987.

10 (*a*) M. Frechette and C. Bensimon, *Inorg. Chem.*, 1995, **34**, 3520; (*b*) L. J. Radonovich and D. M. Glick, *Inorg. Chem.*, 1971, **10**, 1463; (*c*) C. J. Kepert, L. Wei-Min, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1994, **47**, 365–384; (*d*) L. I. Semenova and A. H. White, *Aust. J. Chem.*, 1999, **52**, 507–517; (*e*) C. J. Kepert, L. Wei-Min, L. I. Semenova, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1999, **52**, 481–496; (*f*) L. I. Semenova, A. N. Sobolev, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1999, **52**, 519–529; (*g*) M. G. B. Drew, P. B. Iveson, M. J. Hudson, J. O. Liljenzin, L. Spjuth, P-Yves Cordier, A. Enarsson, C. Hill and C. Madic, *J. Chem. Soc., Dalton Trans.*, 2000, 821; (*h*) M. G. B. Drew, M. J. Hudson, P. B. Iveson, C. Madic and M. L. Russell, *J. Chem. Soc., Dalton Trans.*, 2000, 2711.

11 (*a*) R. F. Bryan, P. T. Greene, P. F. Stokely and E. W. Wilson, Jr., *Inorg. Chem.*, 1971, **10**, 1468; (*b*) H. Bauer, J. Blanc and D. L. Ross, *J. Am. Chem. Soc.*, 1964, **86**, 5125; (*c*) L. R. Melby, N. J. Rose, E. Abramson and J. C. Caris, *J. Am. Chem. Soc.*, 1964, **86**, 5117; (*d*) C. C. Hinckley, *J. Am. Chem. Soc.*, 1969, **91**, 5160; (*e*) M. F. Richardson, W. F. Wagner and D. E. Sands, *Inorg. Chem.*, 1968, **7**, 2495; (*f*) J. A. Cunningham, D. E. Sands, W. F. Wagner and M. R. Richardson, *Inorg. Chem.*, 1969, **8**, 22; (*g*) E. D. Watkins, II, J. A. Cunningham, T. Phillips, II, D. E. Sands and W. F. Wagner, *Inorg. Chem.*, 1969, **8**, 29; (*h*) M. C. Favas, D. L. Kepert, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1980, 454.

12 Z. Otwinowski and W. Minor, in *Methods in Enzymology, 276*, ed. C. W. Carter, Jr. and R. M. Sweet, Academic Press, New York, 1997, pp. 307–326.

13 S. Mackay, C. J. Gilmore, C. Edwards, N. Stewart and K. Shankland, maXus Computer Program for the Solution and Refinement of Crystal Structures, Nonius, The Netherlands, MacScience, Japan and The University of Glasgow, 1999.

14 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.

15 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Gottingen, Germany, 1997.

16 G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1997.

17 K. Iftikhar, M. Sayeed and N. Ahmad, *Inorg. Chem.*, 1982, **21**, 80.

18 A. R. Al-Karaghouli and J. S. Wood, *Inorg. Chem.*, 1972, **11**, 2293.

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

20 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 3rd edn., 1978.

21 (*a*) Y. Ihara, Y. Fukuda and K. Sone, *Inorg. Chem.*, 1987, **26**, 3745; (*b*) Y. Ihara, Y. Fukuda and K. Sone, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1825; (*c*) A. B. P. Lever, E. Montovani and B. S. Ramaswamy, *Can. J. Chem.*, 1971, **49**, 1957.