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Structural variety in nitrate complexes of the heavy lanthanides with 2,2′:6′,2″-terpyridine, and stereoselective replacement of nitrate

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Structural studies show that the solvolysis of a nitrate group in the heavy lanthanide complexes [Ln(terpy)(NO_3)$_3$] {Ln = Yb, Lu; terpy = 2,2′:6′,2″-terpyridine} is stereoselective. In the complexes [Ln(terpy)(NO_3)$_3$(EtOH)], the ‘equatorial nitrate group’, which lies in the same plane as the terpy ligand, coordinates in a monodentate fashion and the vacant coordination site is filled by an ethanol molecule. Similarly, in the unusual complexes [Yb(terpy)(NO_3)$_2$(H_2O)$_2$][NO_3] and [Lu(terpy)(NO_3)$_2$(H_2O)(EtOH)][NO_3], two water molecules or a water and an ethanol molecule are bound to the metal in preference to the nitrate and lie in the same plane as the terpy ligand.

Introduction

Nitrate complexes of the lanthanides are of considerable current interest for the separation of lanthanides and actinides in nuclear waste from reprocessing spent fuel by solvent extraction. Use of N- and O-donor ligands, rather than the traditional phosphorus-containing ligands, affords totally incinerable secondary waste. One approach employs amide ligands,[1] another uses tridentate N-donors such as 2,2′:6′,2″-terpyridine.[2] Lanthanide nitrate complexes of terpy were first reported by Sinha;[3] since then, several groups have made a systematic study of this area and have found that the choice of solvent and lanthanide ion can have a significant effect on the geometry of the complexes.[4–7] For the early and central members of the lanthanide series, a range of formulations and coordination geometries, including [Ln(terpy)(NO_3)$_3$(H_2O)] with three bidentate nitrates, [Ln(terpy)$_2$(NO_3)$_2$]$^+$[Ln(terpy)(NO_3)$_4$]$^-$ and [Ln(terpy)(NO_3)$_2$(H_2O)$_2$]$^+$[NO_3]$^-$ with two bidentate nitrates, [Ln(terpy)(NO_3)$_3$(H_2O)]·terpy and [Ln(terpy)(NO_3)$_3$(H_2O)] with two bidentate and one unidentate nitrate, and [Ln(terpy)(NO_3)$_3$] with three bidentate nitrates, have all been characterised.[6,7]

In a related series of studies, we have investigated the coordination properties of terpyridine nitrate complexes of ytterbium and lutetium, the smallest of the lanthanide ions. We now describe the results and show that in these complexes there is a preference for the replacement of the ligands opposite to the terpy ligand in the ‘equatorial plane’ of the complex.

Results and discussion

Reaction of hot solutions of hydrated [Ln(NO_3)$_3$] (Ln = Yb, Lu) and terpy in dry MeCN yields colourless crystals of [Ln(terpy)(NO_3)$_3$] {Ln = Yb (**1**), Lu (**2**)} on cooling. The structure of **1** has been reported previously,[7] and an X-ray analysis of **2** reveals that this complex is isomorphous and isostructural with **1**. The molecular structure of **2** is illustrated in Fig. 1, while selected bond parameters are listed in Table 1. In each complex, the metal is nine-coordinate. The complexes contain an almost planar terpy ring and three bidentate nitrate groups bound to the metal. There is little sign of asymmetry in the Ln–O bonds,

Table 1 Selected bond lengths (Å) and angles (°) for **2**

Lu(1)–N(1)	2.395(2)	Lu(1)–N(2)	2.379(2)
Lu(1)–N(3)	2.407(2)	Lu(1)–O(41)	2.440(2)
Lu(1)–O(42)	2.350(2)	Lu(1)–O(51)	2.394(2)
Lu(1)–O(52)	2.364(2)	Lu(1)–O(61)	2.360(2)
Lu(1)–O(62)	2.370(2)		
O(41)–N(4)–O(42)	115.1(2)	O(41)–N(4)–O(43)	122.8(2)
O(42)–N(4)–O(43)	122.1(2)	O(51)–N(5)–O(52)	114.8(2)
O(51)–N(5)–O(53)	122.4(2)	O(52)–N(5)–O(53)	122.8(2)
O(61)–N(6)–O(62)	115.7(2)	O(61)–N(6)–O(63)	122.0(2)
O(62)–N(6)–O(63)	122.3(2)		

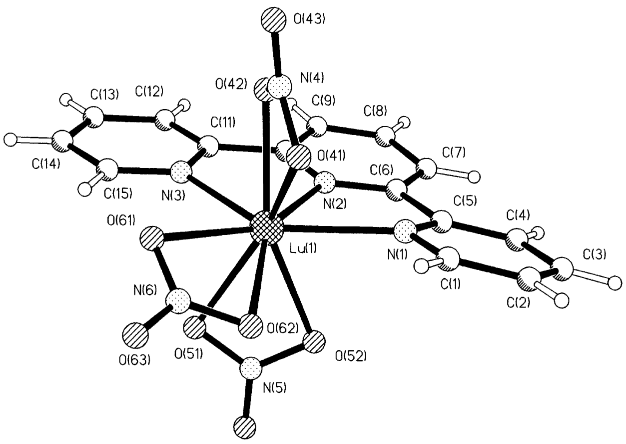

Fig. 1 The molecular structure of [Lu(terpy)(NO_3)$_3$] (**2**), showing the atom numbering scheme.

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Table 2 Selected bond lengths (Å) and angles (°) for **3** and **4**

	3 (Ln = Yb)	**4** (Ln = Lu)
Ln(1)–N(1)	2.462(4)	2.477(3)
Ln(1)–N(2)	2.457(4)	2.455(3)
Ln(1)–N(3)	2.446(4)	2.444(3)
Ln(1)–O(1)	2.355(3)	2.346(3)
Ln(1)–O(2)	2.486(4)	2.482(3)
Ln(1)–O(4)	2.447(4)	2.444(3)
Ln(1)–O(5)	2.370(3)	2.382(3)
Ln(1)–O(7)	2.261(4)	2.279(3)
Ln(1)–O(10)	2.301(4)	2.297(3)
O(1)–N(4)–O(2)	116.5(4)	116.0(3)
O(1)–N(4)–O(3)	120.6(4)	121.5(4)
O(2)–N(4)–O(3)	122.9(5)	122.5(4)
O(4)–N(5)–O(5)	115.5(4)	116.2(3)
O(4)–N(5)–O(6)	122.7(4)	122.4(5)
O(5)–N(5)–O(6)	121.8(6)	121.4(5)
O(7)–N(6)–O(8)	119.1(5)	120.8(4)
O(7)–N(6)–O(9)	113.9(16)	116.8(4)
O(8)–N(6)–O(9)	122.6(17)	122.4(4)
Ln(1)–O(7)–N(6)	138.9(3)	138.4(3)
Ln(1)–O(10)–C(16)	136.2(6)	135.9(3)

as there is in [Sc(terpy)$(NO_3)_3$],[4] presumably owing to the larger radius of the Ln^{3+} ion.

In contrast, if the synthesis is carried out in absolute ethanol, a different colourless crystalline product can be isolated from the reaction. This has been characterised crystallographically as [Ln(terpy)$(NO_3)_3$(EtOH)] {Ln = Yb (**3**), Lu (**4**)}. Complexes **3** and **4** are isostructural and are isomorphous with the previously characterised erbium analogue.[5] They are also structurally similar to the complex [Tm(terpy)$(NO_3)_3(H_2O)$],[7] which contains a coordinated water molecule instead of ethanol. The molecular structure of **4** is shown in Fig. 2 and selected bond parameters for **3** and **4** are listed in Table 2. The similarity between the formal +3 ionic radii for these two adjacent lanthanide elements is reflected by the similarities in the Ln–N and Ln–O bond lengths (Ln = Yb, Lu). A comparison of the two sets show differences that are of the same order of magnitude as the estimated standard deviations associated with them. The ligand bond parameters in the two complexes are, as expected, also similar. The structures of **3** and **4** are related to those of **1** and **2** through the replacement of a bidentate nitrate group *trans* to the terpy ligand by a monodentate nitrate group and a coordinated ethanol linked by an intramolecular hydrogen bond; in **3** the O(8) ··· H(10A) distance is 2.07 Å and the O(8) ··· H(10A)–O(10) angle 139.1°, while in **4**, the parameters are similar, with the O(8) ··· H(10A) distance is 2.03 Å and the O(8) ··· H(10A)–O(10) angle 152.6°.

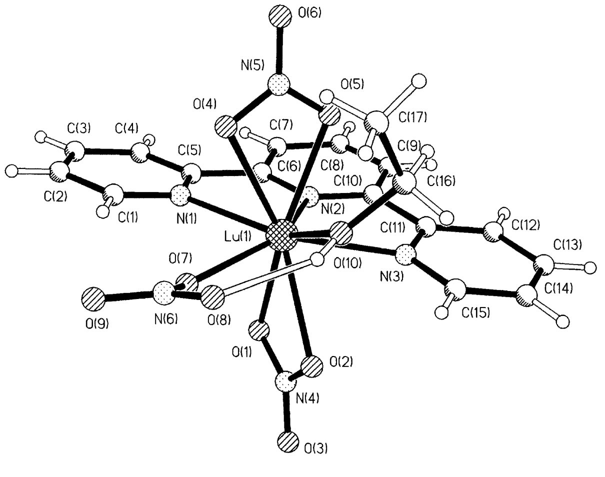

Fig. 2 The molecular structure of [Lu(terpy)$(NO_3)_3$(EtOH)] (**4**), showing the atom numbering scheme.

Table 3 Selected bond lengths (Å) and angles (°) for **5** and **6**

	5 (Ln = Yb)	**6** (Ln = Lu)
Ln(1)–N(1)	2.468(6)	2.456(6)
Ln(1)–N(2)	2.483(5)	2.465(6)
Ln(1)–N(3)	2.464(6)	2.474(7)
Ln(1)–O(1)	2.390(5)	2.388(5)
Ln(1)–O(2)	2.471(5)	2.403(5)
Ln(1)–O(4)	2.403(5)	2.373(5)
Ln(1)–O(5)	2.431(5)	2.487(5)
Ln(1)–O(10)	2.270(5)	2.307(5)
Ln(1)–O(11)	2.319(5)	2.315(5)
O(1)–N(4)–O(2)	114.8(6)	115.6(5)
O(1)–N(4)–O(3)	122.7(6)	123.3(6)
O(2)–N(4)–O(3)	122.5(6)	121.1(6)
O(4)–N(5)–O(5)	115.2(6)	115.1(5)
O(4)–N(5)–O(6)	122.0(7)	121.6(6)
O(5)–N(5)–O(6)	122.7(6)	123.3(6)
O(7)–N(6)–O(8)	121.2(6)	121.9(9)
O(7)–N(6)–O(9)	118.8(6)	117.4(8)
O(8)–N(6)–O(9)	120.0(7)	120.6(9)
Ln(1)–O(10)–C(16)	—	130.7(5)

If these compounds are recrystallised from water, or the synthesis is carried out in wet ethanol, in addition to **3** and **4**, the colourless products [Yb(terpy)$(NO_3)_2(H_2O)_2$][NO_3]·$2H_2O$ (**5**) and [Lu(terpy)$(NO_3)_2(H_2O)$(EtOH)] [NO_3]·EtOH (**6**), respectively, are obtained. These complexes have also been characterised crystallographically. In both complexes, the metals remain nine-coordinate. The diaqua species [Ln(terpy)$(NO_3)_2$-$(H_2O)_2$][NO_3]·$2H_2O$ (Ln = Tb, Lu and Y), analogous to **5**, have been structurally characterised previously, and the bond parameters for **5** (Table 3) are in close agreement with those reported, allowing for the general reduction in metal–ligand bond lengths in going from left to right across the lanthanide series.[6] However, lanthanide complexes with the formulation of **6** have not been characterised previously. The molecular structure of **6** is illustrated in Fig. 3, while selected bond parameters for **5** and **6** are listed in Table 3. Here, one water molecule and one ethanol molecule have replaced the 'equatorial' nitrate group in **2**. While the metal atom remains nine-coordinate, the presence of the coordinated water and ethanol molecules, and of the ion-separated nitrate group, leads to a change in the hydrogen-bonding pattern. In contrast to the structure of **4**, in **6**, the ethanolic proton, H(10), forms an intermolecular hydrogen bond with an oxygen atom, O(7), of the free nitrate [H(10A) ··· O(7) 1.757 Å, O(10)–H(10A) ··· O(7) 172.5°]. A proton on the coordinated water molecule acts as a hydrogen-bond donor, with an interaction to an oxygen of a coordinated nitrate in an adjacent molecule [H(11B) ··· O(5) 2.03 Å; O(5) is related by the symmetry operation $2 - x$, $1 - y$, $-z$). In terms

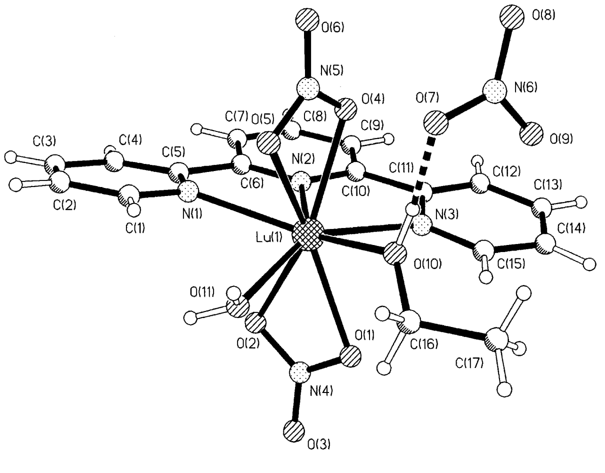

Fig. 3 The structure of [Lu(terpy)$(NO_3)_2(H_2O)$(EtOH)][NO_3] (**6**), showing the atom numbering scheme.

of a structural comparison between **5** and **6**, there is a greater difference in metal–ligand bond lengths between the two structures than that observed for **3** and **4**, but, overall, these differences are only marginally greater than the associated errors and reflect the similarity in radii between $\mathrm{Lu^{3+}}$ and $\mathrm{Yb^{3+}}$. The small differences may be related to the differences induced in the metal coordination sphere by the replacement of two water molecules with a water and an ethanol molecule.

The replacement of one water by an ethanol molecule leading to the coordination to the same metal of both water and an alcohol molecule is rare, but not unprecedented {*c.f.* $[\mathrm{La(NO_3)_3(OH_2)_2(MeOH)(bipy)}]\cdot$(15-crown-5)}.[8] In this reaction, the high concentration of ethanol permits the solvolysis of the Ln–$\mathrm{ONO_2}$ bond rather than the Ln–O(H)Et bond.

In **5** and **6**, the coordinated water and/or ethanol molecules lie *trans* to the terpy group and the "T-shaped" (terpy)Ln$\mathrm{(O_2NO)_2}$ unit remains essentially unaltered throughout the changes. Other workers reacted *in situ*-prepared $[\mathrm{Yb(terpy)(NO_3)_3}\cdot x\mathrm{H_2O}]$ with Hacac and found that the $[\mathrm{Yb(terpy)(O_2NO)_2(acac)}]$ (acac = acetylacetonato) complex formed displays a similar "T-shaped" structural arrangement for the (terpy)Ln$\mathrm{(O_2NO)_2}$ unit.[9] The consistency in the geometry of the (terpy)Ln$\mathrm{(O_2NO)_2}$ moiety in the structures of **1**–**6** may be illustrated by comparing the structures. An example of this is shown in Fig. 4, where the structures of **1** and **5** are superimposed. The structure of the diaqua complex **5** is shown in solid lines and the structure of the trinitrate **1** is shown in dashed lines. Apart from a slight twist of the axial nitrate groups, the structures are very similar, even the orientation of the two water molecules mirrors the orientation of the 'equatorial' nitrate.

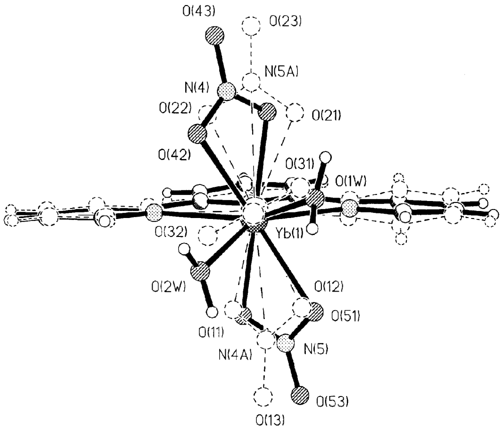

Fig. 4 Superimposition of the structures of $[\mathrm{Yb(terpy)(NO_3)_3}]$ (**1**) (dashed lines) and $[\mathrm{Yb(terpy)(NO_3)_2(H_2O)_2}]^+$ (**5**) (solid lines).

The consistent breaking of Ln–O bonds involving the nitrate group *trans* to the terpy ligand appears to be a general phenomenon in all these compounds. In $[\mathrm{Yb(terpy)(NO_3)_3}]$ (**1**), the Yb–O bonds in the group *trans* to the terpy ligand average 2.376 Å, compared to an average of 2.395 Å for the four other Yb–O bonds, thus the lability does not reflect thermodynamic weakening. Similarly, in **2**, the Lu–O average distance for the nitrate group *trans* to the terpy ligand, at 2.365 Å, is shorter than the average Lu–O distance for the two axial nitrate groups (2.387 Å). The coordinated terpyridyl ligand apparently produces a kinetic weakening in the Ln–O bond *trans* to it. Whilst the solid-state structure need not reflect the course of reaction in solution, a possible explanation would involve the approach of electron-rich nucleophiles to the side of the complex ion away from the electron-rich terpyridyl ligand. In the complexes **3**–**6**, it is also noteworthy that the Ln–O distances of the monodentate nitrate/water, the two water and the water/ethanol molecules, respectively, are somewhat shorter than the distances for the 'equatorial' nitrates in **1** and **2** and the axial nitrates in all the structures.

Conclusion

The apparent preferred replacement of the 'equatorial' nitrate group by solvent molecules in this series of lanthanide complexes may point to the availability of these equatorial sites for 'favoured' replacement by other ligands that will lead to orientational control in lanthanide coordination chemistry. There is increased interest in incorporating lanthanide complexes into coordination polymers,[10] and the implementation of 'favoured' coordination replacement in these complexes may lead to the 'engineering' of new materials.

Experimental

Hydrated lanthanide nitrates, terpyridyl and solvents were obtained as commercial products (Aldrich) and were used without further purification.

Preparation of $[\mathrm{Ln(terpy)(NO_3)_3}]$ {Ln = Yb(1), Lu(2)}

Hot solutions of $[\mathrm{Ln(NO_3)_3}\cdot x\mathrm{H_2O}]$ (0.13 g; 0.29 mmol) in acetonitrile (10 ml) and terpy (0.07 g; 0.3 mmol) in acetonitrile (10 ml) were mixed. Colourless needle crystals formed on standing for a few hours. Analysis: $[\mathrm{Yb(terpy)(NO_3)_3}]$, found C, 29.22; H, 1.97; N, 14.68; required: C, 30.42; H, 1.87; N 14.19%. $[\mathrm{Lu(terpy)(NO_3)_3}]$, C, 29.51; H, 1.88; N, 14.10; required: C, 30.32; H, 1.87; N, 14.14%.

Preparation of $[\mathrm{Ln(terpy)(NO_3)_3(EtOH)}]$ {Ln = Yb(3), Lu(4)}

Hot solutions of $[\mathrm{Ln(NO_3)_3}\cdot x\mathrm{H_2O}]$ (0.13 g; 0.29 mmol) in ethanol (10 ml) and terpy (0.07 g; 0.3 mmol) in ethanol (10ml) were mixed. Colourless diamond-shaped crystals formed on standing for a few hours. Analysis: $[\mathrm{Yb(terpy)(NO_3)_3(EtOH)}]$, found: C, 27.84; H, 2.68; N, 12.68; required C, 31.98; H, 2.68; N, 12.68%.

Preparation of $[\mathrm{Yb(terpy)(NO_3)_2(H_2O)_2}][\mathrm{NO_3}]\cdot 2\mathrm{H_2O}$ (5) and $[\mathrm{Lu(terpy)(NO_3)_2(H_2O)(EtOH)}][\mathrm{NO_3}]\cdot\mathrm{EtOH}$ (6)

Complex **5** was obtained on crystallising **1** from water or by adding a small quantity of water (1 $\mathrm{cm^3}$) to the solutions used for the synthesis of **1**. A single crystal of $[\mathrm{Lu(terpy)(NO_3)_2(H_2O)(EtOH)}][\mathrm{NO_3}]$ was serendipitously discovered among a bulk sample of $[\mathrm{Lu(terpy)(NO_3)_3}]\cdot\mathrm{EtOH}$.

Microanalyses were obtained for a selection of the compounds, but tended to be misleading. With the facilities available, no special precautions could be taken in handling the compounds prior to microanalysis and it is believed that loss of coordinated ethanol occurred (unprotected crystals rapidly deteriorated on exposure to air). The susceptibility of the $[\mathrm{Ln(terpy)(NO_3)_3}]$ complexes to attack by water has been demonstrated by Semenova and White,[6] and variable composition of the complexes of terpy with nitrates of the heavier lanthanides (between zero and three water molecules per $[\mathrm{Ln(terpy)(NO_3)_3}]$) was reported by Sinha.[3] Taken together, these two factors would account for the unreliable microanalyses. Our crystallographic results give us confidence in the composition of these compounds, however.

Crystallography

Details of the data collection and processing, structure determination, and refinement for the five reported structures are summarised in Table 4. Diffraction experiments were performed either on a Nonius Kappa CCD diffractometer (for **2**, **3** and **5**) or on a Bruker AXS SMART diffractometer (for **4** and **6**) on Station 9.8 at the CLRC Daresbury synchrotron. Both

Table 4 Data collection, structure solution and refinement data for complexes **2**–**6**

	2	**3**	**4**	**5**	**6**
Formula	$C_{15}H_{11}LuN_6O_9$	$C_{17}H_{17}N_6O_{10}Yb$	$C_{17}H_{17}LuN_6O_{10}$	$C_{15}H_{17}N_6O_{12}Yb$	$C_{19}H_{25}LuN_6O_{12}$
Formula weight	594.27	638.41	640.34	646.39	704.42
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	9.0435(4)	8.680(1)	8.7235(2)	8.897(1)	8.682(7)
b/Å	16.5688(6)	21.877(1)	21.9191(3)	10.981(1)	12.260(11)
c/Å	13.2564(6)	11.299(1)	11.3386(4)	20.950(1)	13.482(1)
α/°	90	90	90	90	66.13(5)
β/°	108.591(3)	91.59(1)	91.649(2)	92.87(1)	82.96(6)
γ/°	90	90	90	90	69.99(6)
V/Å^3	1882.69(14)	2144.8(3)	2167.17(10)	2044.2(3)	1258.4(18)
Z	4	4	4	4	2
T/K	180	180	150	180	150
λ/Å	0.71069	0.71069	0.6887	0.71069	0.6887
μ/mm^{-1}	5.309	4.429	4.623	4.655	3.996
Meas./Indep. reflect.	47367/4289	7217/3735	14776/5825	5509/3532	9612/6585
Data used [$I. > 2\sigma(I)$]	3929	3280	5138	3016	3735
R_1 (obs. data)	0.0211	0.028	0.0338	0.051	0.0535
wR_2 (all data)	0.0455	0.063	0.0925	0.098	0.1056

diffractometers were equipped with an Oxford Cryosteam crystal cooling apparatus. The data sets were corrected for Lorentz and polarization effects and for absorption. The structures were solved by heavy atom methods (SHELXS 86[11] for **2**, **3** and **5**, and SHELXTL[12] for **4** and **6**) and refined by full-matrix least-squares on F^2 using SHELXL 97,[13] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were placed on the relevant carbon atoms using AFIX constraints and allowed to ride on the carbon atom position. Ethanolic and water hydrogen atoms were either located in the electron density difference maps and refined with restraints or placed in geometrically idealised positions and allowed to ride on the oxygen atom positions. In the structure of **3**, one of the oxygen atoms of the monodentate nitrate group suffered from positional disorder and was refined over two sites with the partial occupancies summing to unity. In each refinement, a weighting scheme that produced a relatively flat analysis of variance was introduced and refinement continued until convergence was reached.

CCDC reference numbers 169191–169195.

See http://www.rsc.org/suppdata/dt/b2/b200480c/ for crystallographic data in CIF or other electronic format.

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References

1 B. M. Rapko, B. K. McNamara, R. D. Rogers, G. J. Lumetta and B. P. Hay, *Inorg. Chem.*, 1999, **38**, 2455; P. B. Iveson, M. G. B. Drew, M. J. Hudson and C. Madic, *J. Chem. Soc., Dalton Trans.*, 1999, 3605.
2 M. G. B. Drew, M. J. Hudson, P. B. Iveson, C. Madic and M. L. Russell, *J. Chem. Soc., Dalton Trans.*, 1999, 2433.
3 S. P. Sinha, *Z. Naturforsch., A.*, 1965, **20**, 1661.
4 A. M. Arif, F. A. Hart, M. B. Hursthouse, M. Thornton-Pett and W. Zhu, *J. Chem. Soc., Dalton Trans.*, 1984, 2449.
5 S. A. Cotton and P. R. Raithby, *Inorg. Chem. Commun.*, 1999, **2**, 86.
6 L. I. Semenova and A. H. White, *Aust. J. Chem.*, 1999, **52**, 507.
7 M. G. B. Drew, P. B. Iverson, M. J. Hudson, J. O. Liljenzin, L. Spjuth, P.-Y. Cordier, A. Enarsson, C. Hill and C. Madic, *J. Chem. Soc., Dalton Trans.*, 2000, 821.
8 Z. P. Ji and R. D. Rogers, *J. Chem. Crystallogr.*, 1994, **24**, 415.
9 K. Hayashi, N. Nagao, K. Harada, M. Haga and T. Fukuda, *Chem. Lett.*, 1998, 1173.
10 S. Tanase, M. Andruh, A. Müller, M. Schmidtmann, C. Mathonière and G. Rombaut, *Chem. Commun.*, 2001, 1084.
11 G. M. Sheldrick, SHELXS 86, Program for Crystal Structure Solution, University of Göttingen, Germany, 1986.
12 G. M. Sheldrick, SHELXTL Manual, version 5, Bruker AXS Inc., Madison, WI, 1994.
13 G. M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.