DALTON

Novel octadecanuclear copper(II)–lanthanoid(III) clusters. Synthesis and structures of $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)][ClO_4]_{17}\cdot 16H_2O$ (Ln^{III} = Gd^{III} or Sm^{III})

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Two octadecanuclear clusters $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)][ClO_4]_{17}\cdot 16H_2O$ (Ln^{III} = Gd^{III} or Sm^{III}) have been synthesized and characterized by X-ray structural analysis. The clusters are isostructural, crystallizing in the triclinic space group $P\bar{1}$ with $Z = 1$. In each structure six Ln^{III} are positioned at the vertices of an octahedron with twelve Cu^{II} at the midpoints of the edges of the octahedron. The 24 OH^- groups act as μ_3 bridges each ligating one Ln^{III} and two Cu^{II}. The octahedron encapsulates an unusual $\mu_{12}\text{-}ClO_4^-$ anion of which each oxygen atom co-ordinates to three Cu^{II} at the axial positions. Ten of the $C_5H_5N^+CH_2CH_2CO_2^-$ ligands act in the μ-carboxylato-*O,O′* mode, while the other two act in the carboxylato-*O,O′* mode each chelating a Ln^{III}, resulting in different co-ordination environments for the Cu^{II} and Ln^{III}.

Polynuclear mixed-metal clusters are of special current interest. The nature of the magnetic exchange interactions between transition and lanthanoid metal ions with bridging ligands has attracted considerable interest both theoretically and as regards possible applications.[1–3] These kinds of compounds are also possible precursors to high-temperature superconductors.[4] Very recently polynuclear metal complexes have also been reported to serve as hosts for small molecules or ions.[5–9]

Recently advantage of the zwitterionic characteristic of betaine ($Me_3N^+CH_2CO_2^-$) has been taken to overcome the charge-compensation problem in attaching carboxylate ligands to a copper(II) centre, giving an interesting tetracarboxylate complex $[Cu(O_2CCH_2NMe_3)_4][NO_3]_2$.[10] The stable $[Cu(O_2CCH_2NMe_3)_4]^{2+}$ core can be used as a 'metallo-ligand' to bind other hard metal ions such as Ca^{II} and Li^{I}.[11] Encouraged by this fact, we have attempted to synthesize mixed-metal Cu^{II}–Ln^{III} complexes containing carboxylate bridges using $Me_3N^+CH_2CO_2^-$ and its derivatives, and have succeeded in the preparation of some polynuclear complexes containing it or its derivative pyridinioacetate ($C_5H_5N^+CH_2CO_2^-$).[12] Much more interesting is the fact that, when we increased the pH value of the Cu^{II}–Ln^{III}–$C_5H_5N^+CH_2CO_2^-$ reaction system to ≈3.5 several polynuclear $Cu^{II}{}_{12}Ln^{III}{}_6$ (Ln = Nd, Gd. *etc.*) clusters were isolated, $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(\mu\text{-}O_2CCH_2NC_5H_5)_{12}(H_2O)_{18}(\mu_{12}\text{-}ClO_4)][ClO_4]_{17}\cdot nH_2O$.[13] We have now extended our study to polynuclear $Cu^{II}{}_{12}Ln^{III}{}_6$ compounds containing a higher analogue namely pyridiniopropionate ($C_5H_5N^+CH_2CH_2CO_2^-$). X-Ray diffraction analysis has shown that although such clusters have analogous $Cu^{II}{}_{12}Ln^{III}{}_6$ cores to those found in the $C_5H_5N^+CH_2CO_2^-$ clusters, some of the $C_5H_5N^+CH_2CH_2CO_2^-$ ligands behave differently upon co-ordination, resulting in different environments about the Cu^{II} and Ln^{III}. In this paper we report the synthesis and crystal structures of two clusters, $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)][ClO_4]_{17}\cdot 16H_2O$, where Ln^{III} = Gd^{III} **1** or Sm^{III} **2**, respectively.

Experimental

Pyridiniopropionate was synthesized with the literature method.[14] All other reagents were commercially available and used as received. The C, H and N microanalyses were carried out with a Perkin-Elmer elemental analyser. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Nicolet 5DX spectrometer.

CAUTION: Metal perchlorates are potentially explosive. Only a small amount of material should be prepared and handled with great care.

Preparation of compounds

$[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)][ClO_4]_{17}\cdot 16H_2O$ 1. A mixture of $C_5H_5N^+CH_2CH_2CO_2^-$ (0.5 g, 3 mmol) and $Cu(NO_3)_2\cdot 6H_2O$ (0.12 g, 0.5 mmol) was dissolved in distilled water (3 cm^3) and heated at 60 °C for 10 min. An aqueous solution (2 cm^3) of $Gd(NO_3)_3\cdot 6H_2O$ (0.44 g, 1 mmol) was then added followed by an aqueous solution (2 cm^3) of $NaClO_4\cdot H_2O$ (0.7 g, 5 mmol) with stirring for 20 min. The resulting deep blue solution was adjusted to pH ≈ 3.5 by very slow addition of 0.1 mol dm^{-3} aqueous NaOH, and then the solution was allowed to evaporate slowly at room temperature. After about 10 d grey-blue polyhedral crystals began to appear, and the product was collected within 1 month (*ca.* 15% yield) (Found: C, 18.55; H, 3.10; N, 2.80. Calc. for $C_{96}H_{196}Cl_{18}Cu_{12}Gd_6N_{12}O_{152}$: C, 18.45; H, 3.15; N, 2.65%). IR ($\tilde{\nu}$/cm^{-1}): 3430s (br), 3128w, 3050m, 2966w, 2931w, 1623vs, 1574s, 1489s, 1440s, 1405s, 1321w, 1300w, 1145vs, 1110vs, 1082vs, 948w, 878w, 779m, 681s, 632s, 596w and 575m.

$[Cu_{12}Sm_6(\mu_3\text{-}OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)][ClO_4]_{17}\cdot 16H_2O$ 2. This complex was synthesized by the above procedure with $Sm(NO_3)_3\cdot 6H_2O$ instead of $Gd(NO_3)_3\cdot 6H_2O$. The yield was *ca.* 10% (Found: C, 18.30; H, 3.10; N, 2.50. Calc. for $C_{96}H_{196}Cl_{18}Cu_{12}N_{12}O_{152}Sm_6$: C, 18.45; H, 3.15; N, 2.70%). IR data ($\tilde{\nu}$/cm^{-1}): 3388vs (br), 3085m, 2973w, 1637vs, 1588s, 1489s, 1405s (br), 1318w, 1300w, 1145vs, 1110vs, 1089vs, 990w, 948w, 878w, 772w, 681m, 625s and 519m.

X-Ray crystallography

A summary of crystallographic data for complexes **1** and **2** is given in Table 1. Data were collected on an Enraf-Nonius

CAD4 diffractometer using graphite-monochromated Mo-Kα (λ = 0.710 69 Å) radiation at 294 K. For both complexes, determination of the crystal class, orientation matrix, and cell dimensions was performed according to established procedures; the intensity data were collected using the ω–2θ scan (5.0° min^{-1}) mode.[15] Two standard reflections were monitored after every 200 data measurements, showing only small random variations (< 1.5%). Data processing was with the NRCVAX program package.[16]

Most of the non-hydrogen atoms in complexes **1** and **2** were located by direct methods with the SHELXS 86 program package[17] and subsequent Fourier syntheses were used to derive the remaining non-hydrogen atoms. All the non-hydrogen atoms were refined anisotropically except the two-fold disordered oxygen atoms of the perchlorate anions in both complexes, which were subjected to geometric restraints. The weighting schemes were $w = 1/[\sigma^2(F_o^2) + (0.0992P)^2]$ for complex **1** and $1/[\sigma^2(F_o^2) + (0.0925P)^2 + 73.6P]$ for complex **2**, where $P = [\max.(F_o^2,0) + 2F_c^2]/3$. Hydrogen atoms of water molecules were not located from the difference maps; those of the $C_5H_5N^+CH_2CH_2CO_2^-$ ligands were generated geometrically (C–H 0.96 Å) and assigned isotropic thermal parameters, riding on their parent carbon atoms. All the hydrogen atoms were held stationary and included in the final stage of full-matrix least-squares refinement using the SHELXL 93 program package.[18] Selected bond lengths and angles are listed in Table 2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/54.

Results and Discussion

X-Ray crystallography has established that crystals of complexes **1** and **2** are isostructural; each consists of discrete $[Cu_{12}Ln_6(OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(ClO_4)]^{17+}$ cations, perchlorate anions and lattice water molecules. A stereoview of the cation in **1** is illustrated in Fig. 1, which may be best described in terms of a $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}]^{18+}$ core of pseudo-cubic O_h symmetry with six Gd^{III} positioned at the vertices of a regular octahedron and twelve Cu^{II} located at the midpoints of the twelve octahedral edges, as shown in Fig. 2. The polyhedron of twelve Cu^{II} may be viewed as a cuboctahedron which is capped on the six square faces by the six Gd^{III}. This Gd–Cu metal fragment is interconnected by 24 similar $\mu_3\text{-}OH^-$ ligands that are each linked to one Gd^{III} and two Cu^{II} such that each $Gd(\mu_3\text{-}OH)_4$ fragment is square pyramidal and each $Cu(\mu_3\text{-}OH)_4$ fragment is square planar. The most interesting finding is the encapsulated $\mu_{12}\text{-}ClO_4^-$ anion at the centre of the $Cu^{II}_{12}Gd^{III}_6$ octahedral cage. As shown in Fig. 3, this perchlorate anion exhibits the very rare 12-co-ordination mode of XO_4^{n-}-anions. Each of the four oxygen atoms is connected to three Cu^{II} [Cu–O 2.263(9)–2.420(10) Å], resulting in a pseudo-tetrahedral symmetry. The $[Cu_{12}Ln_6(\mu_3\text{-}OH)_{24}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)]^{17+}$ skeleton in **1** is very similar to those found in the analogous $Cu^{II}_{12}Ln^{III}_6$ clusters containing $C_5H_5N^+CH_2CO_2^-$ ligands.[13] The $\mu_3\text{-}OH^-$ groups in **1** resemble those of a few reported examples of μ_3-hydroxo-bridges found in cubane-like transition or lanthanoid metal

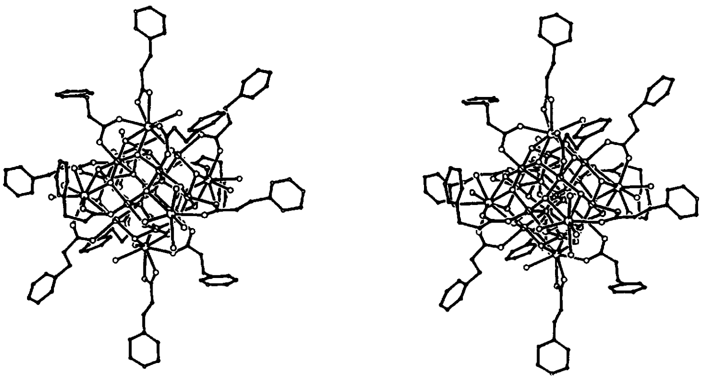

Fig. 1 Stereoview of the structure of the $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(O_2CCH_2CH_2NC_5H_5)_{12}(H_2O)_{16}(\mu_{12}\text{-}ClO_4)]^{17+}$ cation in complex **1**

Table 1 Crystallographic data for complexes **1** and **2***

	1	**2**
Formula	$C_{96}H_{196}Cl_{18}Cu_{12}Gd_6N_{12}O_{152}$	$C_{96}H_{196}Cl_{18}Cu_{12}Sm_6N_{12}O_{152}$
M	6294.73	6253.33
a/Å	17.731(6)	17.751(5)
b/Å	17.999(8)	18.001(7)
c/Å	18.678(4)	18.689(5)
α/°	72.78(4)	72.73(4)
β/°	63.96(4)	64.08(4)
γ/°	76.93(6)	76.95(4)
U/Å^3	5084(6)	5097(6)
D_c/Mg m^{-3}	2.056	2.037
μ/mm^{-1}	3.513	3.280
F(000)	3110	3098
Crystal size/mm	0.28 × 0.30 × 0.40	0.30 × 0.40 × 0.40
θ Range/°	1.4–24	1.4–25
Reflections collected	16 017	17 860
Unique data with $I > 3\sigma(I)$	11 920	15 505
Data, parameters	11 920, 1194	15 505, 1194
Goodness of fit on F^2	1.062	1.109
Final R_1 (wR_2)	0.0662 (0.1709)	0.0658 (0.1764)

* Details in common: triclinic, space group $P\bar{1}$; Z = 1.

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

	1	2		1	2
Ln(1)–O(42)	2.430(6)	2.438(7)	Cu(2)–O(4)	2.290(8)	2.32(3)
Ln(1)–O(12)	2.435(6)	2.445(7)	Cu(3)–O(10h)	1.961(5)	1.946(7)
Ln(1)–O(4h)	2.439(5)	2.442(7)	Cu(3)–O(11h)	1.969(5)	1.945(7)
Ln(1)–O(5h)	2.437(6)	2.457(7)	Cu(3)–O(9h)	1.981(5)	1.982(7)
Ln(1)–O(1h)	2.445(6)	2.463(6)	Cu(3)–O(3h)	1.994(5)	1.980(7)
Ln(1)–O(2w)	2.490(7)	2.500(8)	Cu(3)–O(21)	2.348(7)	2.338(8)
Ln(1)–O(3w)	2.501(6)	2.499(8)	Cu(3)–O(2)	2.39(2)	2.32(3)
Ln(1)–O(12h)	2.515(5)	2.522(7)	Cu(4)–O(12h)	1.951(6)	1.938(7)
Ln(1)–O(1w)	2.556(6)	2.577(8)	Cu(4)–O(1h)	1.972(5)	1.968(7)
Ln(2)–O(22)	2.380(7)	2.394(7)	Cu(4)–O(31)	2.246(6)	2.243(8)
Ln(2)–O(10h)	2.407(5)	2.431(7)	Cu(4)–O(4)	2.331(11)	2.23(3)
Ln(2)–O(3h)	2.457(5)	2.480(7)	Cu(5)–O(4h)	1.966(6)	1.949(7)
Ln(2)–O(2h)	2.470(6)	2.484(7)	Cu(5)–O(1h)	1.986(5)	1.977(7)
Ln(2)–O(62)	2.488(6)	2.492(8)	Cu(5)–O(41)	2.281(6)	2.283(8)
Ln(2)–O(4w)	2.507(5)	2.513(8)	Cu(5)–O(3)	2.417(13)	2.47(3)
Ln(2)–O(61)	2.513(5)	2.517(7)	Cu(6)–O(12h)	1.966(6)	1.973(7)
Ln(2)–O(6h)	2.518(6)	2.538(7)	Cu(6)–O(5h)	1.977(5)	1.966(7)
Ln(3)–O(52)	2.406(6)	2.427(8)	Cu(6)–O(8h)	1.982(5)	1.985(7)
Ln(3)–O(8h)	2.436(6)	2.436(7)	Cu(6)–O(11h)	1.992(6)	1.993(7)
Ln(3)–O(11h)	2.437(5)	2.463(7)	Cu(6)–O(51)	2.337(7)	2.359(8)
Ln(3)–O(9h)	2.468(5)	2.482(7)	Cu(6)–O(4)	2.349(14)	2.37(3)
Ln(3)–O(7w)	2.482(7)	2.486(8)	O(1)–Cu(6a)	2.331(10)	2.30(2)
Ln(3)–O(5w)	2.483(6)	2.504(9)	O(1)–Cu(1a)	2.350(7)	2.31(2)
Ln(3)–O(8w)	2.481(6)	2.502(8)	O(1)–Cu(3a)	2.351(12)	2.43(2)
Ln(3)–O(6w)	2.490(7)	2.503(8)	O(2)–Cu(5a)	2.326(10)	2.27(3)
Ln(3)–O(7h)	2.505(6)	2.517(7)	O(2)–Cu(4a)	2.328(9)	2.45(4)
Cu(1)–O(4h)	1.942(6)	1.948(7)	O(3)–Cu(2a)	2.263(9)	2.23(2)
Cu(1)–O(3h)	1.952(6)	1.956(7)	O(2h)–Cu(2a)	1.968(6)	1.950(7)
Cu(1)–O(5h)	2.001(5)	1.994(7)	O(2h)–Cu(4a)	1.981(5)	1.986(7)
Cu(1)–O(6h)	2.007(5)	2.010(7)	O(6h)–Cu(2a)	1.969(6)	1.960(7)
Cu(1)–O(3)	2.309(11)	2.27(2)	O(7h)–Cu(5a)	1.982(5)	1.977(7)
Cu(1)–O(11)	2.317(6)	2.333(8)	O(9h)–Cu(5a)	1.967(6)	1.967(7)
Cu(2)–O(8h)	1.937(6)	1.956(7)	O(10h)–Cu(4a)	1.951(6)	1.958(7)
Cu(2)–O(7h)	1.982(6)	1.971(7)			
O(42)–Ln(1)–O(12)	84.3(2)	85.1(3)	O(5h)–Cu(1)–O(6h)	179.4(2)	179.5(3)
O(42)–Ln(1)–O(4h)	74.7(2)	74.8(3)	O(4h)–Cu(1)–O(3)	76.2(4)	78.5(6)
O(12)–Ln(1)–O(4h)	74.2(2)	74.6(2)	O(3h)–Cu(1)–O(3)	102.4(4)	100.8(6)
O(42)–Ln(1)–O(5h)	140.1(2)	139.8(2)	O(5h)–Cu(1)–O(3)	103.5(3)	104.1(5)
O(12)–Ln(1)–O(5h)	74.9(2)	75.1(2)	O(6h)–Cu(1)–O(3)	75.9(3)	75.5(5)
O(4h)–Ln(1)–O(5h)	67.2(2)	66.6(2)	O(4h)–Cu(1)–O(11)	88.3(2)	87.9(3)
O(42)–Ln(1)–O(1h)	74.6(2)	138.6(3)	O(3h)–Cu(1)–O(11)	92.9(2)	92.7(3)
O(12)–Ln(1)–O(1h)	139.0(2)	74.8(2)	O(5h)–Cu(1)–O(11)	86.3(2)	86.4(3)
O(4h)–Ln(1)–O(1h)	66.6(2)	65.3(2)	O(6h)–Cu(1)–O(11)	94.3(2)	94.0(3)
O(5h)–Ln(1)–O(1h)	99.6(2)	97.6(2)	O(3)–Cu(1)–O(11)	160.9(3)	162.0(5)
O(42)–Ln(1)–O(2w)	139.3(2)	140.2(3)	O(8h)–Cu(2)–O(7h)	84.4(2)	84.4(3)
O(12)–Ln(1)–O(2w)	82.2(2)	82.2(3)	O(8h)–Cu(2)–O(4)	75.8(4)	77.7(8)
O(4h)–Ln(1)–O(2w)	136.3(2)	136.2(3)	O(7h)–Cu(2)–O(4)	106.1(3)	109.1(9)
O(5h)–Ln(1)–O(2w)	71.4(2)	71.7(3)	O(10h)–Cu(3)–O(11h)	176.5(3)	176.4(3)
O(1h)–Ln(1)–O(2w)	135.4(2)	135.0(2)	O(9h)–Ln(3)–O(7h)	64.9(2)	64.4(2)
O(42)–Ln(1)–O(3w)	80.4(2)	80.4(3)	O(7w)–Ln(3)–O(7h)	135.8(2)	135.5(3)
O(12)–Ln(1)–O(3w)	140.1(2)	140.9(3)	O(5w)–Ln(3)–O(7h)	72.5(2)	72.7(3)
O(4h)–Ln(1)–O(3w)	134.6(2)	133.9(3)	O(8w)–Ln(3)–O(7h)	72.1(2)	72.3(2)
O(5h)–Ln(1)–O(3w)	135.9(2)	135.4(3)	O(6w)–Ln(3)–O(7h)	128.6(2)	129.0(3)
O(1h)–Ln(1)–O(3w)	70.6(2)	71.1(3)	O(4h)–Cu(1)–O(3h)	178.4(2)	179.2(3)
O(2w)–Ln(1)–O(3w)	85.9(2)	86.2(3)	O(4h)–Cu(1)–O(5h)	86.3(2)	86.1(3)
O(42)–Ln(1)–O(12h)	136.7(2)	136.5(2)	O(3h)–Cu(1)–O(5h)	94.8(2)	94.5(3)
O(12)–Ln(1)–O(12h)	136.8(2)	135.9(2)	O(4h)–Cu(1)–O(6h)	93.7(2)	94.2(3)
O(4h)–Ln(1)–O(12h)	100.5(2)	99.3(2)	O(3h)–Cu(1)–O(6h)	85.1(2)	85.2(3)
O(5h)–Ln(1)–O(12h)	64.2(2)	63.6(2)	O(11h)–Ln(3)–O(7h)	101.9(2)	100.9(2)
O(1h)–Ln(1)–O(12h)	64.6(2)	63.7(2)	O(4h)–Cu(5)–O(41)	88.1(2)	88.1(3)
O(2w)–Ln(1)–O(12h)	72.7(2)	72.9(2)	O(1h)–Cu(5)–O(41)	88.3(2)	89.1(3)
O(3w)–Ln(1)–O(12h)	73.2(2)	73.1(3)	O(4h)–Cu(5)–O(3)	73.2(3)	73.2(10)
O(42)–Ln(1)–O(1w)	71.0(2)	72.0(3)	O(1h)–Cu(5)–O(3)	101.2(3)	100.7(9)
O(12)–Ln(1)–O(1w)	73.4(2)	74.6(3)	O(41)–Cu(5)–O(3)	158.1(3)	147.8(10)
O(4h)–Ln(1)–O(1w)	134.5(2)	136.0(3)	O(12h)–Cu(6)–O(5h)	83.7(2)	83.5(3)
O(5h)–Ln(1)–O(1w)	131.2(2)	132.2(3)	O(12h)–Cu(6)–O(8h)	95.9(2)	96.2(3)
O(1h)–Ln(1)–O(1w)	128.5(2)	129.3(3)	O(5h)–Cu(6)–O(8h)	176.8(2)	177.6(3)
O(2w)–Ln(1)–O(1w)	68.4(2)	68.3(3)	O(12h)–Cu(6)–O(11h)	178.3(2)	177.9(3)
O(3w)–Ln(1)–O(1w)	66.8(2)	66.5(3)	O(5h)–Cu(6)–O(11h)	94.7(2)	94.4(3)
O(12h)–Ln(1)–O(1w)	125.0(2)	124.6(3)	O(8h)–Cu(6)–O(11h)	85.7(2)	85.9(3)
O(22)–Ln(2)–O(10h)	76.9(2)	76.3(2)	O(12h)–Cu(6)–O(51)	93.0(2)	92.8(3)
O(22)–Ln(2)–O(3h)	75.7(2)	75.5(2)	O(5h)–Cu(6)–O(51)	94.1(2)	94.5(3)
O(10h)–Ln(2)–O(3h)	66.8(2)	65.7(2)	O(8h)–Cu(6)–O(51)	89.2(2)	87.8(3)
O(22)–Ln(2)–O(2h)	141.3(2)	140.7(3)	O(11h)–Cu(6)–O(51)	87.6(3)	87.8(3)
O(10h)–Ln(2)–O(2h)	66.8(2)	66.7(2)	O(1a)–Cu(6)–O(51)	159.8(3)	161.3(6)
O(3h)–Ln(2)–O(2h)	100.6(2)	100.0(2)	O(12h)–Cu(6)–O(4)	76.1(3)	73.9(9)

Table 2 (*continued*)

	1	**2**		**1**	**2**
O(22)–Ln(2)–O(62)	131.2(2)	132.1(3)	O(5h)–Cu(6)–O(4)	103.2(3)	101.8(8)
O(10h)–Ln(2)–O(62)	138.3(2)	139.1(3)	O(8h)–Cu(6)–O(4)	73.6(3)	75.9(8)
O(3h)–Ln(2)–O(62)	140.3(2)	139.8(3)	O(11h)–Cu(6)–O(4)	103.8(3)	106.1(8)
O(2h)–Ln(2)–O(62)	75.5(2)	75.9(2)	O(51)–Cu(6)–O(4)	158.2(3)	157.5(5)
O(22)–Ln(2)–O(4w)	81.4(2)	82.2(3)	Cu(6a)–O(1)–Cu(1a)	93.0(3)	94.1(5)
O(10h)–Ln(2)–O(4w)	135.5(2)	134.6(2)	Cu(6a)–O(1)–Cu(3a)	91.4(3)	89.8(6)
O(3h)–Ln(2)–O(4w)	70.4(2)	70.5(2)	Cu(1a)–O(1)–Cu(3a)	91.2(3)	89.1(6)
O(2h)–Ln(2)–O(4w)	134.6(2)	134.0(2)	Cu(5a)–O(2)–Cu(4a)	94.4(3)	93.1(11)
O(62)–Ln(2)–O(4w)	84.3(2)	83.8(3)	Cu(5a)–O(2)–Cu(3)	91.9(4)	95.4(9)
O(22)–Ln(2)–O(61)	80.2(2)	81.3(2)	Cu(4a)–O(2)–Cu(3)	92.8(4)	91.7(11)
O(10h)–Ln(2)–O(61)	143.1(2)	144.4(2)	Cu(2a)–O(3)–Cu(1)	92.8(3)	93.9(5)
O(3h)–Ln(2)–O(61)	133.6(2)	134.0(2)	Cu(2a)–O(3)–Cu(5)	89.5(3)	88(1)
O(2h)–Ln(2)–O(61)	122.3(2)	122.4(2)	Cu(1)–O(3)–Cu(5)	91.0(3)	89(1)
O(62)–Ln(2)–O(61)	51.4(2)	51.2(2)	Cu(2)–O(4)–Cu(4)	92.4(3)	93.5(8)
O(4w)–Ln(2)–O(61)	67.2(2)	67.3(3)	Cu(2)–O(4)–Cu(6)	92.6(3)	90.6(9)
O(22)–Ln(2)–O(6h)	138.2(2)	138.2(3)	Cu(4)–O(4)–Cu(6)	90.5(3)	91.9(8)
O(10h)–Ln(2)–O(6h)	99.7(2)	98.4(2)	Cu(4)–O(1h)–Cu(5)	119.3(3)	120.4(4)
O(3h)–Ln(2)–O(6h)	65.2(2)	65.0(2)	Cu(4)–O(1h)–Ln(1)	106.0(3)	106.3(3)
O(2h)–Ln(2)–O(6h)	64.0(2)	63.3(2)	Cu(5)–O(1h)–Ln(1)	103.1(2)	103.6(3)
O(62)–Ln(2)–O(6h)	78.4(2)	78.2(3)	Cu(2a)–O(2h)–Cu(4a)	115.3(3)	114.7(3)
O(4w)–Ln(2)–O(6h)	72.3(2)	72.4(2)	Cu(2a)–O(2h)–Ln(2)	106.7(2)	107.0(3)
O(61)–Ln(2)–O(6h)	116.5(2)	116.6(2)	Cu(4a)–O(2h)–Ln(2)	101.5(3)	101.4(3)
O(52)–Ln(3)–O(8h)	76.1(2)	75.5(3)	Cu(1)–O(3h)–Cu(3)	116.8(3)	116.2(3)
O(52)–Ln(3)–O(11h)	73.6(2)	73.8(3)	Cu(1)–O(3h)–Ln(2)	106.8(2)	106.4(3)
O(8h)–Ln(3)–O(11h)	67.3(2)	67.2(2)	Cu(3)–O(3h)–Ln(2)	101.9(2)	102.4(3)
O(52)–Ln(3)–O(9h)	137.4(2)	136.8(3)	Cu(1)–O(4h)–Cu(5)	119.4(2)	118.8(3)
O(8h)–Ln(3)–O(9h)	97.7(2)	97.2(2)	Cu(1)–O(4h)–Ln(1)	103.8(2)	104.2(3)
O(11h)–Ln(3)–O(9h)	65.4(2)	64.5(2)	Cu(5)–O(4h)–Ln(1)	103.9(2)	105.2(3)
O(52)–Ln(3)–O(7w)	83.8(2)	84.1(3)	Cu(6)–O(5h)–Cu(1)	117.1(2)	117.3(3)
O(8h)–Ln(3)–O(7w)	138.9(2)	138.6(3)	Cu(6)–O(5h)–Ln(1)	107.2(2)	107.7(3)
O(11h)–Ln(3)–O(7w)	72.7(2)	72.8(2)	Cu(1)–O(5h)–Ln(1)	102.1(2)	102.3(3)
O(9h)–Ln(3)–O(7w)	73.7(2)	73.8(2)	Cu(2a)–O(6h)–Cu(1)	112.8(2)	112.1(3)
O(52)–Ln(3)–O(5w)	84.6(2)	84.9(3)	Cu(2a)–O(6h)–Ln(2)	104.9(2)	105.4(3)
O(8h)–Ln(3)–O(5w)	74.9(2)	74.8(3)	Cu(1)–O(6h)–Ln(2)	102.9(2)	103.3(3)
O(11h)–Ln(3)–O(5w)	139.7(2)	139.9(3)	Cu(2)–O(7h)–Cu(5a)	112.5(3)	112.1(3)
O(9h)–Ln(3)–O(5w)	135.2(2)	135.0(3)	Cu(2)–O(7h)–Ln(3)	103.6(2)	103.9(3)
O(7w)–Ln(3)–O(5w)	138.8(2)	139.2(3)	Cu(5a)–O(7h)–Ln(3)	104.0(2)	104.4(3)
O(52)–Ln(3)–O(8w)	139.4(2)	140.2(3)	Cu(2)–O(8h)–Cu(6)	117.7(3)	115.7(3)
O(8h)–Ln(3)–O(8w)	134.9(2)	135.1(3)	Cu(2)–O(8h)–Ln(3)	107.6(2)	107.4(3)
O(11h)–Ln(3)–O(8w)	136.0(2)	135.2(3)	Cu(6)–O(8h)–Ln(3)	103.3(2)	103.7(3)
O(9h)–Ln(3)–O(8w)	73.2(2)	73.3(3)	Cu(5a)–O(9h)–Cu(3)	118.2(3)	118.5(3)
O(7w)–Ln(3)–O(8w)	82.1(2)	82.0(3)	Cu(5a)–O(9h)–Ln(3)	105.9(2)	106.0(3)
O(5w)–Ln(3)–O(8w)	81.5(2)	81.8(3)	Cu(3)–O(9h)–Ln(3)	104.2(2)	104.4(3)
O(52)–Ln(3)–O(6w)	69.7(2)	70.2(3)	Cu(4a)–O(10h)–Cu(3)	121.4(3)	122.4(4)
O(8h)–Ln(3)–O(6w)	131.7(2)	131.5(3)	Cu(4a)–O(10h)–Ln(2)	104.7(2)	104.1(3)
O(11h)–Ln(3)–O(6w)	129.5(2)	130.1(3)	Cu(3)–O(10h)–Ln(2)	104.7(2)	105.3(3)
O(9h)–Ln(3)–O(6w)	130.6(2)	131.3(3)	Cu(3)–O(11h)–Cu(6)	115.5(3)	115.4(3)
O(7w)–Ln(3)–O(6w)	69.9(2)	70.3(3)	Cu(3)–O(11h)–Ln(3)	105.7(2)	106.3(3)
O(5w)–Ln(3)–O(6w)	69.0(2)	69.0(3)	Cu(6)–O(11h)–Ln(3)	102.9(2)	102.5(3)
O(8w)–Ln(3)–O(6w)	69.7(2)	70.0(3)	Cu(4)–O(12h)–Cu(6)	116.1(2)	115.6(4)
O(52)–Ln(3)–O(7h)	138.1(2)	137.7(3)	Cu(4)–O(12h)–Ln(1)	104.2(2)	105.0(3)
O(8h)–Ln(3)–O(7h)	64.4(2)	64.3(2)	Cu(6)–O(12h)–Ln(1)	104.7(2)	105.0(3)

complexes,[19,20] as well as in a tetranuclear Cu_2Dy_2 complex.[2] Each pair of the adjacent non-bonding Cu ··· Cu is linked by a single hydroxide bridge with the Cu ··· Cu distances in range 3.336(3)–3.458(3) Å. Each Gd^{III} is linked to four adjacent Cu^{II} by four μ_3-OH^- bridges with non-bonding Cu ··· Gd separations of 3.461(2)–3.572(3) Å, and each pair of Gd^{III} in each edge of the octahedron is separated at distances of 6.983(1)–7.033(1) Å. Noteworthy is the fact that except for the analogous $C_5H_5N^+$-$CH_2CO_2^-$ clusters,[13] there is only one other known example of a 12-co-ordinate XO_4-type anion.[21] In $[Hg_2(O_4Ge)]$ each oxygen atom of the tetrahedral $[GeO_4]^{4-}$ anion has three non-equivalent bond distances to Hg^{II}.[22] Since the chlorine atom of the present perchlorate anion is located at a crystallographic inverse centre, the oxygen atoms of the anion are required to be distributed over two centrosymmetrically related orientations; the resulting crystal-disordered average geometry of the central $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}(\mu_{12}\text{-}ClO_4)]^{17+}$ kernel thereby conforms ideally to the O_h symmetry.

It is notable that, although large polynuclear transition-metal clusters have been widely investigated and a few bimetallic Cu^{II}–Ln^{III} complexes have been structurally characterized,[1] [4] only several relatively larger $Cu^{II}{}_nLn^{III}{}_2$ clusters have recently been reported,[4] where the maximum metal nuclearity is 10. Thus the mixed (μ_3-hydroxo)(μ-carboxylato-*O*,*O′*)-bridged $Cu^{II}{}_{12}Ln^{III}{}_6$ cation in **1** and the analogous $C_5H_5N^+CH_2CO_2^-$ clusters reported previously constitute the largest among mixed Cu^{II}–Ln^{III} clusters.

The most significant structural difference between cluster **1** and the analogous $C_5H_5N^+CH_2CO_2^-$ cations results from the different ligating modes of the carboxylate groups. In the latter cations all the $C_5H_5N^+CH_2CO_2^-$ ligands act uniquely in the μ-carboxylato-*O*,*O′* mode, each bridging a Cu^{II} and a Ln^{III}. In contrast, only ten of the $C_5H_5N^+CH_2CH_2CO_2^-$ ligands act in the μ-carboxylato-*O*,*O′* mode, while the other two [defined by O(61), O(62), C(61), *etc.* and their symmetry equivalent atoms] act in the carboxylato-*O*,*O′* mode each chelating a Gd^{III}. The

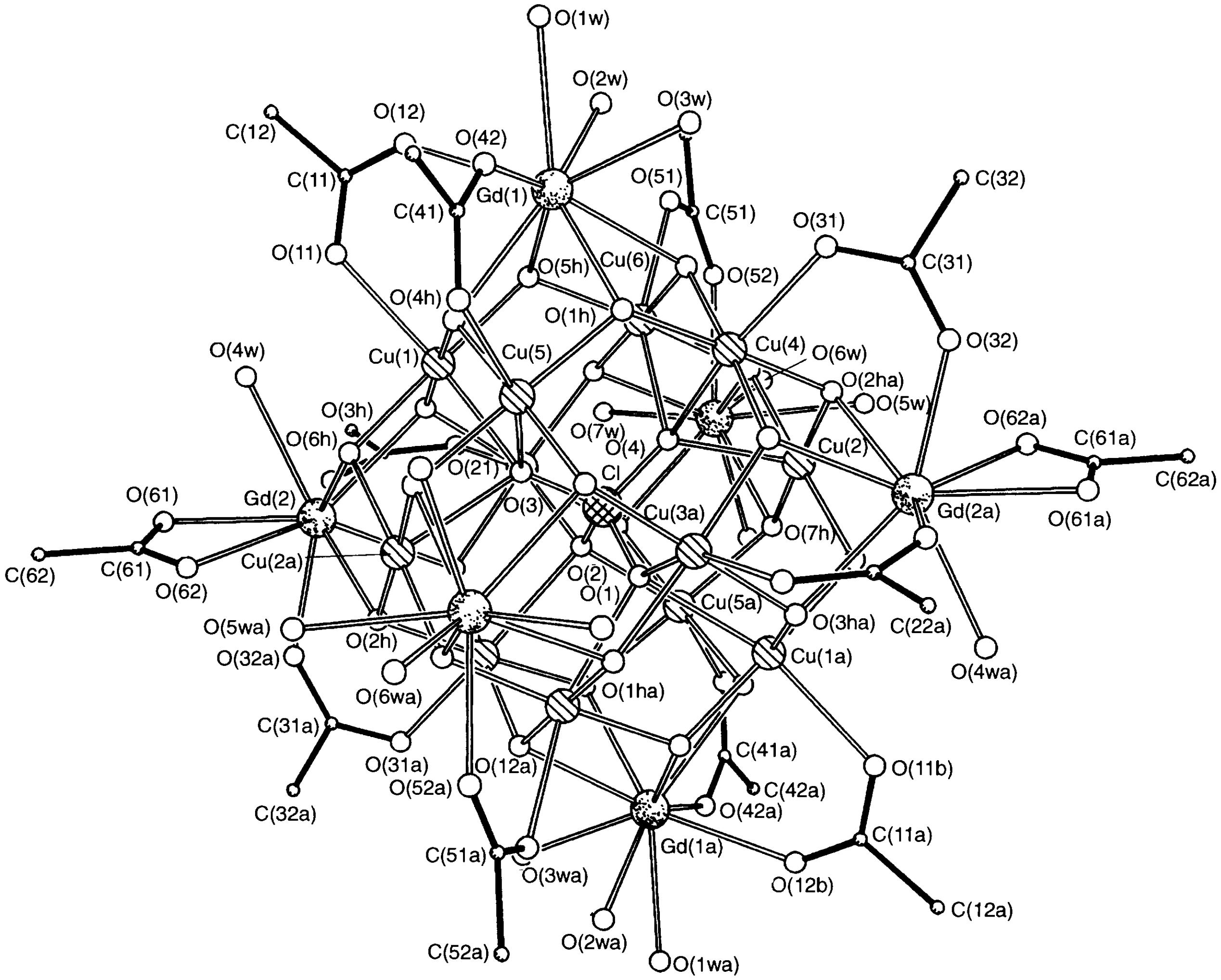

Fig. 2 Perspective view showing the structure of the octadecanuclear cation in complex **1**. For clarity, only the CCO_2 units of $C_5H_5N^+CH_2$-$CH_2CO_2^-$ are shown (solid lines). The Gd atoms are speckled, the Cu atoms are hatched, the Cl atoms are cross-hatched, and the O atoms are open circles. Symmetry code: a $1 - x, 2 - y, -z$

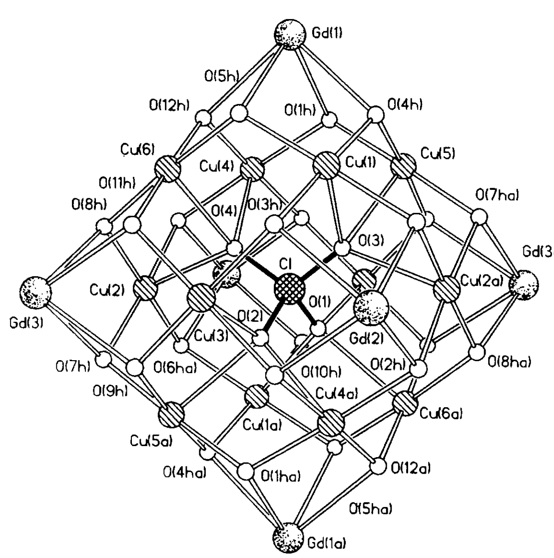

Fig. 3 Perspective view showing the structure of the octahedral cage of $[Cu_{12}Gd_6(\mu_3\text{-}OH)_{24}]^{18+}$ encapsulating a $\mu_{12}\text{-}ClO_4^-$ anion in complex **1**

existence of the two chelated carboxylate groups makes the cation in **1** different from the analogous $C_5H_5N^+CH_2CO_2^-$ cations,[13] and hence it is unique among the $Cu^{II}_{12}Ln^{III}_6$ complexes. The external linkage of one carboxylato oxygen atom to each Cu^{II} of the ten results in a six-co-ordinate oxygen environment about the Cu^{II} with the Cu–O bond lengths characteristic of an elongated octahedron, in which the axial positions are occupied by one carboxy oxygen atom [Cu–O 2.246(6)–2.337(7) Å] and one perchlorate oxygen atom [Cu–O 2.309(11)–2.420(10) Å], while the equatorial positions are occupied by the four $\mu_3\text{-}OH^-$ groups at much shorter Cu–O bond distances [1.942(6)–2.007(6) Å]. Such an elongated octahedral geometry about Cu^{II} has frequently been observed.[23] On the other hand, as a pair of $C_5H_5N^+CH_2CH_2CO_2^-$ ligands ligates the Gd(2) and Gd(2a) atoms in the chelate mode, no carboxy oxygen atom co-ordinates the axial positions of atoms Cu(2) and Cu(2a), resulting in a five-co-ordinate oxygen environment about the two Cu^{II} concomitant with the axial Cu–O bond associated with the $\mu_{12}\text{-}ClO_4^-$ anion having slightly shorter lengths [2.263(9) and 2.290(6) Å for Cu(2a)–O(3) and Cu(2)–O(3), respectively] as compared with those for the six-co-ordinate copper(II) centres. It is noteworthy that no five-co-ordinate copper(II) centre is present in the $C_5H_5N^+$-$CH_2CO_2^-$ clusters. The observation of the chelated $C_5H_5N^+$-$CH_2CH_2CO_2^-$ ligands in **1** may be rationalized on the basis that with the additional methylene group between the carboxy group and the nitrogen atom as compared to $C_5H_5N^+$-$CH_2CO_2^-$ the positively charged nitrogen atom has a much weaker inductive effect on the carboxy group, hence $C_5H_5N^+$-$CH_2CH_2CO_2^-$ has a smaller O–C–O bond angle.[24] This smaller angle may enhance the chelate tendency of the carboxy group toward larger metal ions.[25]

Although all three crystallographically independent Gd^{III} are nine-co-ordinated, each is surrounded by different ligands, different from those in the $C_5H_5N^+CH_2CO_2^-$ cations, which also arise from the different ligation behaviours of $C_5H_5N^+$-$CH_2CH_2CO_2^-$ and $C_5H_5N^+CH_2CO_2^-$ ligands in the octadecanuclear cations. In the $C_5H_5N^+CH_2CO_2^-$ cations each Ln^{III} is co-ordinated by four μ_3-OH^- ligands, three aqua ligands and two oxygen atoms of a pair of μ-carboxylate groups. In contrast, besides the four μ_3-OH^- ligands, the co-ordination environments of the Gd^{III} in **1** are completed by three aqua ligands and two oxygen atoms of a pair of μ-carboxylate groups, by two aqua ligands, one oxygen atom of a μ-carboxylate group and two oxygen atoms of a chelated carboxylate group, and by four aqua ligands and one oxygen atom of a μ-carboxylate group for atoms Gd(1), Gd(2) and Gd(3), respectively. The polyhedron of nine oxygen atoms around each Gd^{III} may be described as a distorted monocapped antiprism, analogous to those found for a large number of nine-co-ordinate lanthanoid(III) complexes.[13,26] The Gd–O (hydroxo) bond lengths are 2.407(5)–2.518(6) Å, Gd–O (aqua) bond lengths 2.481(6)–2.556(6) Å, while Gd–O (carboxy) bond lengths fall in the range 2.380(7)–2.435(6) Å, with the longest ones [2.488(6) and 2.513(5) Å] being associated with the chelated $C_5H_5N^+CH_2CH_2CO_2^-$ ligands.

Since the crystal structure of complex **2** is isostructural with that of **1** only trivial geometric differences are observed between the two clusters. Owing to the slightly different ionic radii of the two lanthanoid(III) ions,[27] the Sm–O bonds in **2** are slightly longer than the corresponding Gd–O bonds in **1**, following the trend in the ionic radii. On the other hand, the corresponding Cu–O bond lengths and O–M–O bond angles are very similar (Table 2). The maximum difference between the corresponding O–M–O bonds is 2.3°, and most have differences of 1°

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References

1 M. Andruh, I. Ramade, E. Codjovi, O. Guillou, O. Kahn and J. C. Trombe, *J. Am. Chem. Soc.*, 1993, **115**, 1822; M. Andruh, O. Kahn, J. Sainto, Y. Dromzee and S. Jeannin, *Inorg. Chem.*, 1993, **32**, 1623; A. Bencini, C. Benelli, A. Caneschi, A. Dei and D. Gatteschi, *Inorg. Chem.*, 1986, **25**, 572; A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128.

2 C. Benelli, A. Caneschi, D. Gatteschi, O. Guillou and L. Pardi, *Inorg. Chem.*, 1990, **29**, 1750.

3 O. Guillou, O. Kahn, R. Oushoorm, K. Boubeker and P. Batail, *Inorg. Chim. Acta*, 1992, **199–200**, 119; R. Georges, O. Kahn and O. Guillou, *Phys. Rev. B*, 1994, **49**, 3235.

4 S. Wang, Z. Pang and D. L. Smith, *Inorg. Chem.*, 1993, **32**, 4992; S. Wang, Z. Pang and M. J. Wagner, *Inorg. Chem.*, 1992, **31**, 5381; D. M. L. Goodgame, D. J. Williams and R. E. Winpenny, *Polyhedron*, 1989, **8**, 1531; A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne and R. E. Winpenny, *J. Chem. Soc., Chem. Commun.*, 1992, 522; A. J. Blake, V. A. Cherepamov, A. A. Dunlop, C. M. Grant, P. E. Y. Milne, J. M. Rawson and R. E. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1994, 2719 and refs. therein.

5 V. W. Day, W. G. Klemperer and O. M. Yaghi, *J. Am. Chem. Soc.*, 1989, **111**, 5959 and refs. therein.

6 Q. Chen and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1994, 1635; Y.-D. Chang, J. Salta and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 325; Q. Chen and J. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1994, 2663; J. Salta, Q. Chen, Y.-D. Chang and J. Zubieta, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 757.

7 A. Müller, M. Penk, R. Rohlfing, E. Krickemeyer and J. Doring, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 926.

8 M. I. Khan and J. Zubieta, *J. Am. Chem. Soc.*, 1992, **114**, 10 058.

9 R. W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Herbst-Irmer, J. Daub, M. Porsch, E. Bill, M. Muther and A. X. Trautwein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1612.

10 X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1991, **10**, 273.

11 X.-M. Chen and T. C. W. Mak, *Polyhedron*, 1994, **13**, 1087; *Inorg. Chem.*, 1994, **33**, 2444.

12 Y.-L. Wu, Y.-X. Tong, Y.-S. Yang and X.-M. Chen, *Acta Sci. Nat. Univ. Sunyatseni*, 1995, **34**, 36.

13 X.-M. Chen, S. M. J. Aubin, Y.-L. Wu, Y.-S. Yang, T. C. W. Mak and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1995, **117**, 9600.

14 X.-M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1991, 3253.

15 B. A. Frenz, The Enraf-Nonius CAD4 SDP—A Real-Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination Package, Enraf-Nonius, Delft, 1978.

16 E. J. Gabe, Y. Le Page, J.-P. Charland and F. C. Lee, *J. Appl. Crystallogr.*, 1989, **22**, 384.

17 G. M. Sheldrick, SHELXS 86, Program for X-Ray Crystal Structure Solution, University of Göttingen, 1986.

18 G. M. Sheldrick, SHELXL 93, Program for X-Ray Crystal Structure Refinement, University of Göttingen, 1993.

19 L. Akhter, W. Clegg, C. D. Garner and D. Collison, *Inorg. Chem.*, 1985, **24**, 1725; P. L. Dedert, J. A. Ibers, T. J. Marks and T. Sorrell, *Inorg. Chem.*, 1982, **21**, 3506; J. Sletten, A. Sorensen, M. Julve and Y. Journaux, *Inorg. Chem.*, 1990, **29**, 5054; J. A. Real, G. D. Munno, R. Chiappetta, M. Julve, F. Lloret, Y. Journaux, J.-C. Colin and G. Blondin, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1184.

20 J. C. Plakatouras, I. Baxter, M. B. Hursthouse, K. M. A. Malik, J. McAleese and S. R. Drake, *J. Chem. Soc., Chem. Commun.*, 1994, 2455; X.-M. Chen and Y.-L. Wu, unpublished work.

21 B. J. Hathaway, *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 2, pp. 413–434.

22 K.-F. Hesse and W. Eysel, *Acta Crystallogr., Sect. A*, 1981, **37**, 429.

23 B. J. Hathaway, in *Comprehensive Coordination Chemistry*, eds. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon, Oxford, 1987, vol. 5, p. 612.

24 X.-M. Chen and T. C. W. Mak, *Struct. Chem.*, 1993, **4**, 247.

25 M.-Y. Chow, X.-M. Chen and T. C. W. Mak, *J. Chem. Soc., Dalton Trans.*, 1993, 3413.

26 A. Ouchi, Y. Susuki, Y. Ohki and Y. Koizumi, *Coord. Chem. Rev.*, 1988, **92**, 29; F. Ribot, P. Toledano and C. Sabchez, *Inorg. Chim. Acta*, 1991, **185**, 239; E. Moret and J.-C. G. Bunzli, *Inorg. Chim. Acta*, 1990, **178**, 83; A. E. Koziol, B. Klimek, K. Stepniak, Z. Rzazynska, O. I. Bodak, L. G. Akselrud, V. V Pavlyuk and V. A. Tafeenko, *Z. Kristallogr.*, 1992, **200**, 25; J.-F. Ma, Z.-S. Jin and J.-Z. Ni, *Acta Chim. Sin.*, 1993, **51**, 784; Z.-B. Duan, Z.-S. Jin, H.-N. Hu and J.-Z. Ni, *Jiegou Huaxue*, 1989, **8**, 168; H.-D. Zeng and K.-Z. Pan, *Jiegou Huaxue*, 1992, **11**, 388; D.-L. Zhang, C.-H. Huang, G.-X. Xu, Q.-T. Zheng and C.-H. He, *Wuji Huaxue Xuebao*, 1992, **8**, 22.

27 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.

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