

Structure of the centred icosahedral samarium cluster formed by bis(l-prolinato)nickel(ii) ligands

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The centred icosahedral twelve-coordinate samarium cluster formed by six bis(l-prolinato)nickel(ii) ligands is synthesized and its crystal structure determined.

Heteronuclear and/or polynuclear complexes are interesting materials due to their structures and properties. Various preparation methods have been proposed in order to obtain such polynuclear complexes. One such method was the preparation of complexes from the interaction of two or more moles of *cis*-[M(am)₄(OH)₂]⁺ [where (am)₄ is a single tetradentate amine ligand, two bidentate amines, or four monodentate amines] with metal halides; ^{1–4} the bis-hydroxo complexes which are used as ligands can be coordinated to the other metals *via* the hydroxo oxygen atoms. Recently Winpenny and coworkers have reported studies where they have attempted to link mononuclear and/or small polynuclear compounds into larger units; especially, they have been exploring the coordination chemistry of ligands derived from 2-hydroxypyridine (2-pyridone) with first-row transition metals.^{5–12} In this work, an amino acid complex was used as a ligand in order to synthesize a new heteronuclear complex.

Amino acids have two or more types of coordination atoms and can act as various bridging ligands.^{13–19} Taking advantage of the properties of the amino acid ligands, the synthesis of an amino acid bridging heterometal complex was applied. A lanthanoid ion, a hard acid, and a bis-amino acidato complex were chosen for the purpose of preparing the heterometal complex, and they were mixed in a non-aqueous solvent with poor coordination ability.

The samarium–nickel complex containing bis(l-prolinato)-nickel(ii) moieties [Ni(pro)₂]: synthesized according to a modified published procedure for Cu(pro)₂²⁰ was prepared by reacting 1 mmol of samarium perchlorate dissolved in 20 cm³ of methanol with a six-fold excess of [Ni(pro)₂]. Evaporation of the solvent gave purple tetrahedral crystals of [Sm{Ni(pro)₂}₆][ClO₄]₃·6MeOH.[†]

Four ClO₄[−] ion sites must exist in the unit cell, since the crystals are cubic (space group: *F*23) and the ClO₄[−] ions lie on the three-fold axes. However, this contradicts the result of gravimetric analysis for ClO₄[−] using tetraphenylarsonium chloride [Found: 12.33%. Calc. for [Sm{Ni(pro)₂}₆][ClO₄]₃·6MeOH, 12.63%]. Therefore, the occupancy of each ClO₄[−] site was fixed at 0.75 when the structure was refined.

The methanol molecules are considered to be loosely trapped in the lattice, as revealed by their extremely large thermal parameters, which leads to immediate decomposition upon filtering.

The coordination environments around the Sm and Ni atoms in the complex is shown in Fig. 1 and a stereoscopic view is shown in Fig. 2. Each nickel atom is surrounded by six atoms: two amino nitrogens, two carboxylate oxygens, which form chelate rings with the nitrogen atoms, and two carboxylate oxygen atoms which link the neighbouring nickel atoms. The samarium atom is coordinated to twelve oxygen atoms. The six Ni(pro)₂ units are coordinated to the icosahedral metal centre *via* two chelating carboxylate oxygen atoms.

By contrast to most twelve-coordinate complexes which are distorted icosahedral owing to restricted ligand bite size, [Sm{Ni(pro)₂}₆]³⁺ shows icosahedral geometry, owing to the larger bite size of the Ni(pro)₂ moieties. All the Sm–O bond lengths are 2.691(3) Å, while the average of the nearest neighbouring O...O is 2.83 Å (ratio O...O/Sm–O = 1.05); angles between two adjacent metal–ligand bonds are in the range 62.8(3)–65.1(1)° (av. = 63.4°); *cf.* ideal icosahedral angle between two adjacent metal(M)–ligand(L) bonds of 63.43° and ideal ratio of L–L/M–L of 1.0515.²¹ Lanthanoid ions capable of forming twelve-coordinate compounds are La³⁺,²²

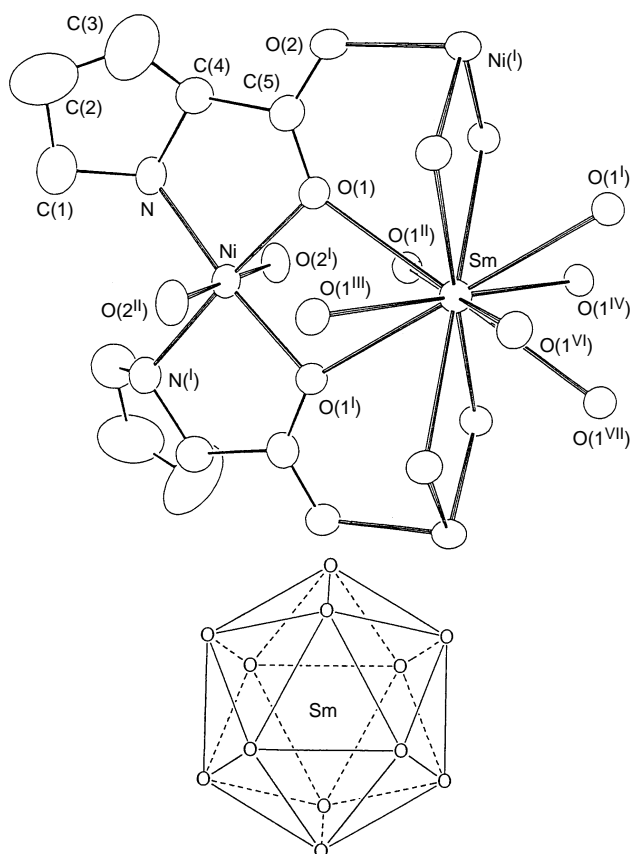


Fig. 1 ORTEP plot around the Sm and Ni atoms in [Sm{Ni(pro)₂}₆]³⁺ showing 50% thermal ellipsoids in the atom numbering scheme. Selected bond distances (Å) and angles (°): Sm–O(1) 2.688(3), Ni–O(1) 2.026(3), Ni–O(2) 2.053(4), Ni–N 2.060(5), O(1)–C(5) 1.295(7), O(2)–C(5) 1.234(7), N–C(1) 1.57(1), N–C(4) 1.496(8), C(1)–C(2) 1.46(2), C(2)–C(3) 1.43(2), C(3)–C(4) 1.37(3), C(4)–C(5) 1.514(8), O(1)–O(1^I) 2.874(7), O(1)–O(1^{II}) 2.77(2), O(1)–O(1^{III}) 2.86(2); O(1)–Sm–O(1^I) 64.6(1), O(1)–Sm–O(1^{II}) 62.0(4), O(1)–Sm–O(1^{III}) 64.3(4), O(1)–Sm–O(1^{IV}) 116.6(1), O(1)–Sm–O(1^V) 115.4(1), O(1)–Sm–O(1^{VI}) 117.11(9), O(1)–Sm–O(1^{VII}) 178.5(5), O(1)–Ni–O(1^I) 90.4(2), O(1)–Ni–O(2) 90.1(4), O(1)–Ni–O(2^{II}) 89.1(4), O(1)–Ni–N 84.4(2), O(1)–Ni–N^I 172.5(4), O(2^{II})–Ni–N 85.4(5), O(2^{II})–Ni–N^I 95.2(5), N–Ni–N^I 101.2(3), Ni–O(1)–C(5) 114.5(4), Ni^I–O(2)–C(5) 123.5(3), O(1)–C(5)–O(2) 126.3(5).

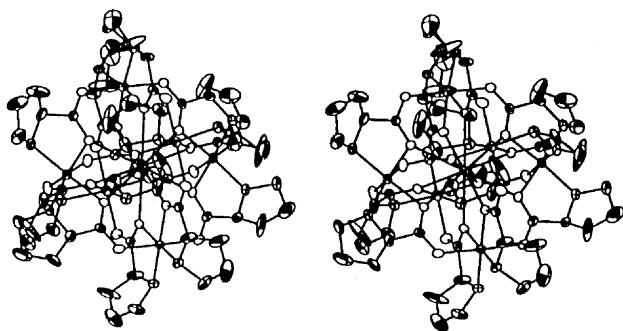


Fig. 2 Stereoscopic view of $[\text{Sm}\{\text{Ni}(\text{pro})_2\}_6]^{3+}$

Ce^{3+} ,²³ Ce^{4+} ,²⁴ Pr^{3+} ,²⁵ and Nd^{3+} ²⁶ whereas it is very difficult to prepare twelve-coordinate complexes of samarium even with NO_3^- . Very recently a 'twelve-coordinate' Sm complex with tris[3-(2-pyridyl)pyrazol-1-yl]hydroborate (L), $[\text{SmL}_2]\text{BPh}_4$, was reported.²⁷ However, half of the twelve Sm–N bond lengths in the complex are extremely long: av. 2.95 Å cf. 2.66 Å (av.) for the shorter set of bonds. Therefore, the complex reported here is very novel. The samarium–oxygen bond lengths in the present complex, 2.691(3) Å, are a little longer than in other eleven- and ten-coordinate samarium complexes,^{28–30} which may arise from restriction imposed by the $6[\text{Ni}(\text{pro})_2]$ cage structure and the high coordination number.

It was confirmed that the icosahedral cluster structure was retained after loss of methanol molecules from the crystals, based on diffraction data of slightly decayed crystals. Moreover, the structure was also retained in alcohol and acetonitrile solutions; UV–VIS spectra of solutions are perfectly consistent with the powder diffuse reflection spectrum. Cyclic voltammetry[‡] of the complex in acetonitrile exhibited reversible waves at ca. -1.5 V and complicated irreversible waves at >0.5 V. The reversible waves imply that Sm^{3+} in the complex shows a Nernstian reduction. The complicated irreversible waves suggest that the nickel atoms interact with each other and that the icosahedral cluster structure may decompose when Ni^{2+} is oxidized to Ni^{3+} in the $\text{Ni}(\text{pro})_2$ units.

Future work will be aimed at investigating the magnetochemistry of this complex.

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Footnotes

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† Crystal data for $[\text{Sm}\{\text{Ni}(\text{pro})_2\}_6][\text{ClO}_4]_3 \cdot 6\text{CH}_3\text{OH}$: purple, tetrahedron, $\text{C}_{66}\text{H}_{120}\text{Cl}_3\text{N}_{12}\text{Ni}_6\text{O}_{42}\text{Sm}$, $M_w = 2363.05$, cubic, space group $F23$ (no. 196), $a = 21.335(2)$ Å, $U = 9710(1)$ Å³, $D_m = 1.64$ g cm⁻³, $D_c = 1.62$ g cm⁻³, $Z = 4$. Based on the systematic absences (hkl : $h+k$, $k+l$, $h+l \neq 2n$), packing considerations, a statistical analysis of the intensity distribution, and the successful solution and refinement of the structure, the space group was determined. Since the absolute configuration of 1-Hpro was known, the structure analysis was based on this configuration. A crystal having approximate dimensions of $0.40 \times 0.30 \times 0.40$ mm was mounted in a glass capillary. All measurements were made on a Rigaku AFC5R diffractometer using the ω - 2θ scan technique to a maximum 2θ value of 60° , with graphite monochromated Mo-K α ($\lambda = 0.71069$ Å) radiation at 20°C . Scans of $(1.55 + 0.30 \tan \theta)^\circ$ were made at a speed of $16.0^\circ \text{min}^{-1}$ (in ω). Of the 2048 reflections which were collected, 1296 were unique ($R_{\text{int}} = 0.053$); equivalent reflections were merged. The linear absorption coefficient, μ , was 19.1 cm^{-1} . An empirical absorption correction based on azimuthal scans of several reflections was applied. This resulted in transmission factors ranging from 0.8920 to 0.9963. The data were corrected for Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient = 1.53190×10^{-7}). The structure was

solved by heavy-atom Patterson methods and expanded using Fourier techniques. The non-hydrogen atoms were anisotropically refined. The final cycle of full-matrix least-squares refinement was based on 769 observed reflections [$I > 3.0\sigma(I)$] and 121 variable parameters and converged at $R = 0.033$ and $R_w = 0.039$. At the final stage of refinement, the difference Fourier map showed minimum and maximum peaks between -0.26 and $+0.22 \text{ e \AA}^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/398.

‡ 5 mmol dm⁻³ $[\text{Sm}\{\text{Ni}(\text{pro})_2\}_6]^{3+}$ in 0.1 mol dm⁻³ tetraethylammonium perchlorate–acetonitrile solution at a glassy carbon disk electrode (scan rate = 200 mV s^{-1}).

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