Synthesis, Molecular and Electronic Structure of Complexes [LNaM^{IV}NaL] (M=Ru,Os; H_3L = 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane)

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The trinuclear complexes [LNaM^{IV}NaL] (M = Ru **1**, Os **2**) where L represents the hexadentate ligand 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane have been synthesized and **1** has been characterized by X-ray crystallography; complex **1** contains an octahedral M$^{IV}S_6$ central core and two trigonal-prismatic terminal LNa units with an N_3S_3 donor set; the electronic structure of the M$^{IV}S_6$ core (M = Ru, Os), has been established as $S = 1$ by temperature-dependent magnetic susceptibility measurements.

Recently we have begun to explore the coordination chemistry of the hexadentate macrocycle 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane (H_3L) with trivalent first-row transition-metal ions.[1] This ligand forms a very stable iron(III) complex, [Fe^{III}L], with an octahedral N_3S_3 donor set.

Cyclic voltammetry revealed that [Fe^{III}L] undergoes a reversible one-electron oxidation at −0.215 V *vs.* ferrocene-ferrocenium (Fc–Fc$^+$) yielding the monocation [FeL]$^+$. Attempts to isolate salts of this cation failed at that time and the question remained open whether this one-electron oxidation is metal-centred yielding Fe^{IV} or if the coordinated ligand is oxidized. Therefore, we decided to synthesize the corresponding complex [Ru^{III}L] and its oxidized form as crystalline solids. The species [RuL]$^+$ is anticipated to be *paramagnetic* if an octahedral Ru^{IV} species is formed ($S = 1$) or, alternatively, to be *diamagnetic* due to antiferromagnetic coupling between a ruthenium(III) ion and a coordinated sulfur radical. In the course of the synthesis we encountered an unexpected preparative result which led to the isolation of novel ruthenium(IV) complex containing a Ru$^{IV}S_6$ core.

When a methanolic reaction mixture of the trisodium salt of the ligand, Na_3L, and [Ru^{II}(dmso)$_4$Cl$_2$](dmso = dimethyl sulfoxide) in the ratio 2:1 was heated to reflux under anaerobic conditions and was then exposed to air a red-black precipitate was obtained. After column chromatography of a CH_2Cl_2 solution two crystalline species were obtained: red-black [LNaRu^{IV}NaL]CH_2Cl_2·MeOH·2H_2O **1** and blue [Ru^{III}L].[†]

The green complex [LNaOs^{IV}NaL] **2** was obtained in a similar fashion by reaction of K_2[Os$^{IV}Cl_6$] and Na_3L in methanol. In this case the presence of [Os^{III}L] was not detectable. Fast atom bombardement mass spectrometry of **1** and **2** in a *m*-nitrobenzylalcohol matrix revealed the molecular-ion peaks at *m/z* 1468.5 for **1** and at 1558.5 for **2** which display the expected isotope distributions due to Ru and Os isotopes. The electronic spectra of solutions of **1** in CH_2Cl_2 and **2** in $CHCl_3$ display many absorption maxima in the visible and near infrared region: **1** 274 nm ($\varepsilon = 5.7 \times 10^4$ dm^3 mol^{-1} cm^{-1}), 538 (5.2×10^3), 646 (1.7×10^3), 952 (1.03×10^4), 1187 (6.6×10^3) 1300 (sh); **2** 314 (4.8×10^4), 409 (4.9×10^3), 435 (sh), 452 (4.8×10^3), 484 (4.8×10^3), 546 (3.0×10^3), 649 (6.05×10^3), 817 (2.4×10^4), 1000 (sh), 1705 (880), 1860 (1.2×10^3).

Fig. 1 shows the structure of the trinuclear neutral molecule in crystals of **1**.[‡] It consists of two sodium ions each in an N_3S_3-donor set provided by the ligand L^{3-} and a central ruthenium(IV) coordinated to six bridging thiolate sulfur donor atoms. The neutral molecule may be perceived as composed of two [NaL]$^{2-}$ units which bind a Ru^{IV} ion *via* two facial S_3-donor sets. Interestingly, the N_3S_3Na polyhedron is trigonal prismatic whereas the RuS_6 core is octahedral. The average Na–N distance is the shortest reported to date for sodium polyamine complexes.[2] The stereochemistry at the Na$^+$ ions is dictated by the steric requirements of the ligand L^{3-} whereas the low-spin t_{2g}^4 electronic configuration of the six coordinate Ru^{IV}-ion favours an octahedral over a trigonal-prismatic arrangement (ligand field stabilization energy). Note that in a recently reported similar structure of [(thf)$_3$Na(μ-SR)$_3$U^{IV}(μ-SR)$_3$Na(thf)$_3$][3] (R = *tert*-butyl, phenyl) the sodium ions are in an octahedral environment of three oxygen and three sulfur donor atoms. The structure of **2** is probably very similar to that of **1**.

Fig. 2 displays the cyclic voltammograms of **1** and **2** recorded in CH_2Cl_2 and $CHCl_3$, respectively. Both species exhibit a reversible one-electron oxidation and a reversible one-electron reduction as was judged from coulometric

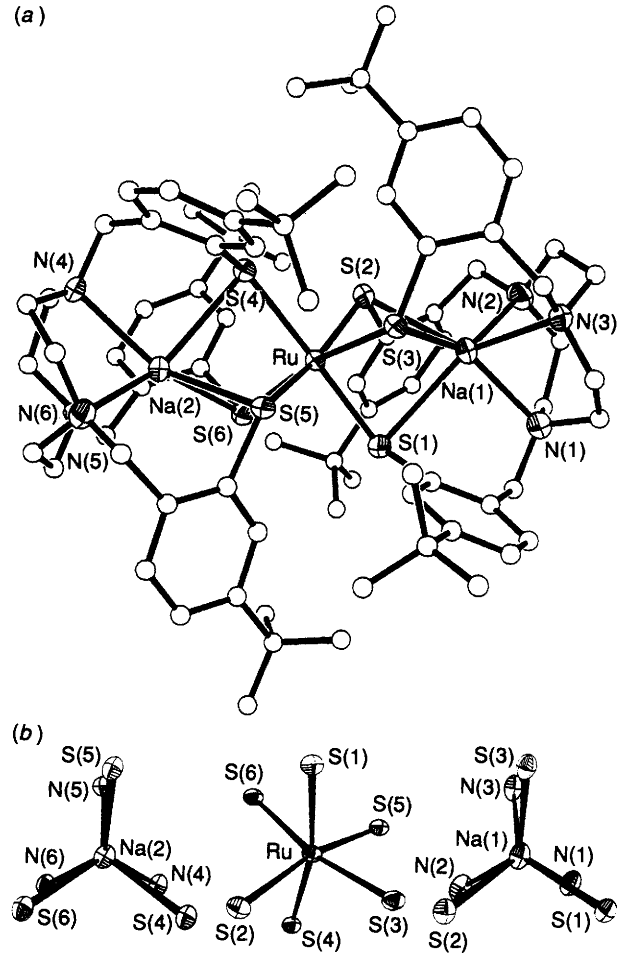

Fig. 1 Structure of the neutral complex in crystals of **1** (*a*) and geometry of metal ion polyhedra (*b*). Selected average bond distances (Å) and angles (°): Ru–S 2.414(2), Na–S 2.751(5), Na–N 2.374(8), Ru(1)···Na(1) 3.352(4), Ru···Na(2) 3.348(3), S(1)–Ru–S(2) 89.4(1), S(2)–Ru–S(3) 88.7(1), S(2)–Ru–S(4) 82.7(1), S(1)–Ru–S(5) 100.1(1), S(3)–Ru–S(5) 84.0(1), S(1)–Ru–S(6) 82.5(1), S(3)–Ru–S(6) 167.7(1), S(5)–Ru–S(6) 88.5(1), S(1)–Ru–S(3) 89.2(1), S(1)–Ru–S(4) 167.2(1), S(3)–Ru–S(4) 100.7(1), S(2)–Ru–S(5) 167.9(1), S(4)–Ru–S(5) 89.1(1), S(2)–Ru–S(6) 100.2(1), S(4)–Ru–S(6) 89.0(1).

measurements at appropriately fixed potentials. The reduction wave most probably involves a metal-centred reduction yielding the negatively charged species [LNaM^{III}NaL]$^-$ (M = Ru, Os) whereas the oxidation to the cationic species [LNaMNaL]$^+$ may be metal-centred (Ru^V, Os^V) or involve one-electron oxidation of the ligand.

Fig. 3 shows the temperature dependent (2–300K) magnetic susceptibility (SQUID-magnetometer, applied field 1T), and effective magnetic moments of powdered samples of **1** and **2**. At elevated temperatures the magnetic moments of **1** approaches the value of *ca.* 3.0 μ_B which is typical for a d^4 ion with t_{tg}^4 ($S = 1$) electronic configuration. At lower temperatures the magnetic moments drop significantly until a nearly diamagnetic ground state is reached. For **2** a nearly temperature-independent paramagnetism is observed from which effective magnetic moments of *ca.* 2.0 μ_B at room temp. *ca.* and of 0.5 μ_B at 10 K are calculated.

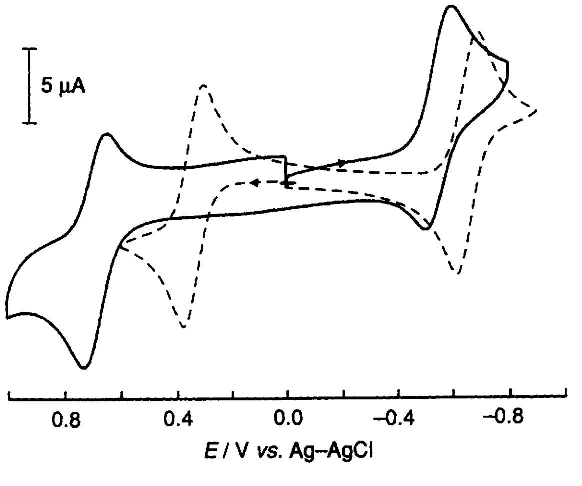

Fig. 2 Cyclic voltammograms of **1** (---) and **2** (———) recorded in CH_2Cl_2 using a Pt-electrode and $CHCl_3$ solution using a glassy carbon electrode, respectively, at a scan rate of 100 mV s^{-1}. Potentials are referenced *vs.* a Ag–AgCl (saturated LiCl;C_2H_5OH) electrode (conditions: [complex] *ca.* 10^{-4} mol dm^{-3}, 0.10 mol dm^{-3} [NBu_4]PF_6 supporting electrolyte).

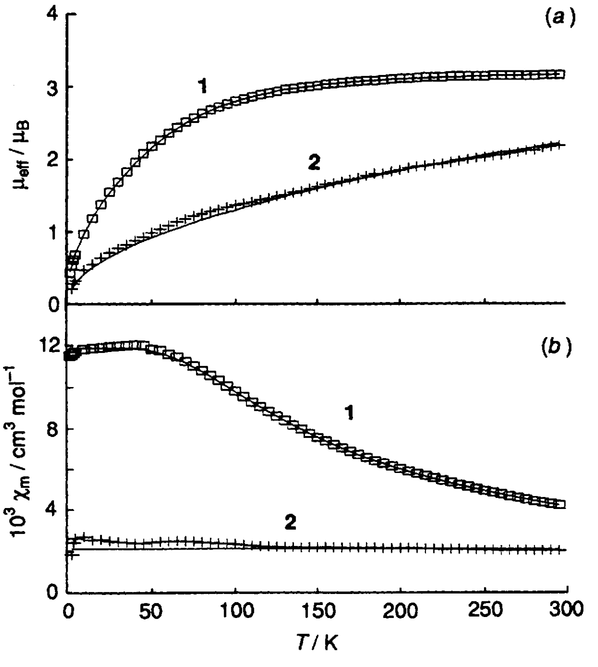

Fig. 3 Temperature dependence of the magnetic moment (*a*) and magnetic susceptibility (*b*) of **1** and **2**. The solid lines represent best fits (see text).

Following the analysis of Oosterhuis and Lang[4] for a complete description of the electronic structure within the t_{2g}^4 configuration, an axial and rhombic perturbation, V_k, of the crystal-field, spin–orbit coupling and the Zeeman interaction with an applied magnetic field H has to be taken into account where ξ is the spin–orbit coupling constant, eqn. (1).

$$\mathscr{H}_1 = \sum_{k=1}^{4} V_k + \xi \sum_{k=1}^{4} \vec{l}_k\vec{s}_k + \mu_B\vec{H} \sum_{k=1}^{4} (\vec{l}_k + 2\vec{s}_k) \qquad (1)$$

The four-electron problem (t_{2g}^4) can be described by a two-hole problem giving the following Hamilton [eqn. (2)].[5]

$$\mathscr{H}_2 = -\sum_{k=1}^{2} V_k - \xi \sum_{k=1}^{2} \vec{l}_k\vec{s}_k + \mu_B\vec{H} \sum_{k=1}^{2} (\vec{l}_k + 2\vec{s}_k) \qquad (2)$$

The energies Δ and V represent the influence of the axial and rhombic crystal field. A positive value for Δ leads to an orbital-singlet as ground state. The above lying orbital doublet is split by V. We have fitted the experimental data (Fig. 3) with parameters Δ, V and ξ for **1** and **2**. In both cases the fit was not sensitive to V. Therefore, V was set to 0 cm^{-1}. For **1** an excellent fit was obtained with values ξ = 1586 cm^{-1} and Δ = 4782 cm^{-1}. The spin–orbit coupling constant agrees very well with a value of *ca.* 1600 cm^{-1} reported for other ruthenium(IV) complexes.[6] A good fit for **2** was obtained when ξ was fixed to 6400 cm^{-1} a value typically found for osmium(IV)[7] and Δ = 14220 cm^{-1}. Such a large spin–orbit coupling constant leads to a temperature-independent susceptibility in the temperature range 2–300 K as is observed. Thus the magnetic data nicely corroborate the assignment of a t_{tg}^4 ($S = 1$) electronic configuration of Ru^{IV} and Os^{IV} in **1** and **2**.

It should be noted that some seven-coordinate ruthenium(IV) complexes of the type [Ru^{IV}(R_2dtc)$_3$](I_3) (R = Me, Et, CH_2Ph; dtc = *N*,*N*-disubstituted dithiocarbamate) and [Ru^{IV}(R_2dtc)$_3$]Cl containing a distorted pentagonal-bipyramidal RuS_6X (X = I, Cl) core have been reported to be diamagnetic with an $S = 0$ ground state.[7]

In a subsequent paper we will describe the synthesis and characterization of the analogous trinuclear [LRuRuRuL]$^{2+}$ and the mononuclear species [M^{III}L] (M = Ru, Os) which shows that the sodium cations in **1** and **2** are readily replaced by other transition-metal ions.

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Footnotes

† The complex [Ru^{III}L] has been fully characterized. The results will be reported elsewhere.

‡ *Crystal data* for **1**: $C_{80}H_{118}Cl_2N_6Na_2O_3RuS_6$; monoclinic, space group $P2_1$, a = 14.217(3), b = 19.705(4), c = 15.071(3) Å, β = 103.11(3)°, U = 4112.3(15) Å^3, Z = 2, D_c = 1.310 g cm^{-3}. A Siemens P4 diffractometer and Mo-Kα radiation (graphite monochromator) was used at 163 K. 8647 Reflections were collected ($3 \leqslant 2\theta \leqslant 52°$), of which 6805 unique data $F \geqslant 4.0\sigma(F)$ were used in refinement. The structure was solved by direct methods; the hydrogen atoms were included with calculated positions with fixed isotopic thermal parameters; all other atoms with anisotropic thermal parameters. Least-squares full-matrix refinement converted to final agreement factors of R = 0.055 and R_w = 0.056 for 884 parameters.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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