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Light-assisted synthesis of a Ru(VI) nitrido complex by the reaction of azide with a Ru(III) complex

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Reaction of Ru(III)(L)(dmf)Cl$_3$ (1) (L = 4,4,4′,4′-tetramethyl-2,2′-bisoxazoline, dmf = *N*,*N*-dimethylformamide) with an excess of sodium azide in a methanol–water mixture leads to the isolation of the sodium salt of a Ru(VI) nitrido complex of the tetraanion of *N*,*N*′-bis-(2,2-dimethyl-1-hydroxyethyl)-1,2-ethanediamide (L′H$_4$; H a dissociable proton) of the formulation Na[Ru(L′)(N)(H$_2$O)]·1.4H$_2$O (2). Complex 2 is not generated in the absence of light. A tentative mechanism for the reaction is proposed and a Ru(IV) intermediate, Na[Ru(L′)(N$_3$)(H$_2$O)]·2CH$_3$OH·2H$_2$O (3), isolated.

Nitrido complexes can be obtained by a variety of routes and the source of N^{3-} ion can be nitriles, ammonia, amido ligands, N$_2$, N$_2$O, NO, azides, *etc.*[1a,2] In this paper we are concerned with the use of the azide ion as the precursor. It is well-known that reaction of azides with metal oxides in the presence of mineral acids yields nitrido complexes, as in reaction (1):[3,4]

$$\mathrm{RuO_4 + NaN_3 + Cl^-} \xrightarrow[\text{8 M HCl}]{} [\mathrm{Ru(N)Cl_5}]^{2-} \qquad (1)$$

In such reactions, azide acts as the reductant as well as the source of the ligated nitrogen. The thermal decomposition of azides to form the nitride ion and dinitrogen has been known for many years.[5] For example, in connection with studies on N$_2$ fixation, in 1969 Chatt and co-workers[6] described a scheme [reaction (2)] for the synthesis of nitrido complexes from lower valent azide precursors:

$$[(\text{ligand})_x\mathrm{M}^{(n)}\text{–N}_3] \rightarrow [(\text{ligand})_x\mathrm{M}^{(n+2)}{\equiv}\mathrm{N}] + \mathrm{N_2} \qquad (2)$$

Although Chatt *et al.* did not succeed in achieving their goal for M = Re(III), Ir(I), Ir(III) and Rh(I),[6] this scheme was later realised by others in the cases of M = Mo(IV)[7] and Cr(III).[8] The decomposition of azide into nitride and N$_2$ is brought about thermally in the case of Mo(IV) and by light in the case of Cr(III). To the best of our knowledge the transformation described by reaction (2) has not been demonstrated for ruthenium. We now wish to report the preparation of a Ru(VI) nitride *via* a Ru(IV) azide intermediate.

Earlier we reported the synthesis and structure of Ru(III)(L)(dmf)Cl$_3$ (**1**, L = 4,4,4′,4′-tetramethyl-2,2′-bisoxazoline, dmf = *N*,*N*-dimethylformamide).[9] The dmf ligand in **1** can be easily replaced by several other monodentate ligands.[9] In an attempt to synthesise a new azide complex of Ru(III), we reacted **1** with an excess of sodium azide in aqueous methanol at room temperature. The solid residue obtained after complete removal of the solvent from the red reaction mixture at room temperature was extracted with the minimum volume of acetonitrile and the extract layered over benzene. After three weeks, yellow crystals of **2** were obtained.

Our X-ray crystallographic studies show that **2** is a sodium salt of a Ru(VI) nitrido complex of the tetraanion of *N*,*N*′-bis-(2,2-dimethyl-1-hydroxyethyl)-1,2-ethanediamide (L′H$_4$; H a dissociable proton) having the formulation Na[Ru(L′)(N)(H$_2$O)]·1.4H$_2$O. The asymmetric unit contains four six-coordinate anionic complexes [Ru(L′)(N)(H$_2$O)]$^-$, one five-coordinate anionic complex [Ru(L′)(N)]$^-$, five sodium ions and eight lattice water molecules. The structure of one of the ordered six-coordinate anions [Ru(L′)(N)(H$_2$O)]$^-$ is shown in Fig. 1 and bond lengths and angles for that anion are given in Table 1. The metric parameters for the other ordered anions are chemically similar, though not necessarily crystallographically indistinguishable. The [Ru(L′)(N)(H$_2$O)]$^-$ anions exhibit a very distorted octahedral coordination about ruthenium with bonds between adjacent ligating atoms falling in the 65–110° range. The tetradentate anionic ligand (L′)$^{4-}$ adopts a bowl configuration in each anion. The angle to the nitride ligand typically falls in the 108–110° range while the angle to the coordinated water lies between 65° and 75°. The four independent Ru–nitride distances in the ordered anions are closely similar, 1.56–1.62(2) Å. The angle formed at the metal by the nitride and water ligands is close to linear, 174–177°. The bonds to the coordinated water molecules are short and one would expect these ligands, trans to nitride, to be labile. It is possible that this may account for the missing water on one of the anions.

A partial crystal packing diagram is shown in Fig. 2. Within the crystal the structure is held in three dimensions mainly by (*i*) interactions between sodium ions and oxygen ions on the anions: Na–O, 2.28–2.53(1) Å; (*ii*) interactions between sodium

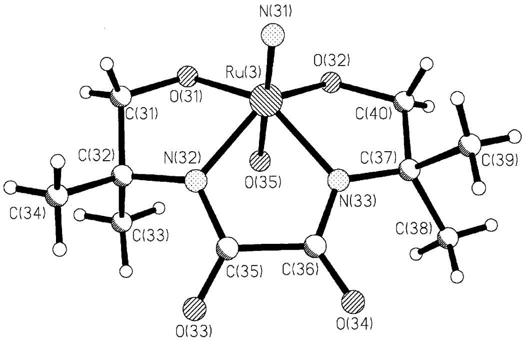

Fig. 1 The structure of one of the anions of Na[Ru(L′)(N)(H$_2$O)] with atom labelling scheme.

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Table 1 Selected bond lengths (Å) and angles (°) for one well-ordered $[Ru(L')(N)(H_2O)]^-$ anion in **2**

Ru3–N31	1.60(2)	Ru3–N32	1.974(11)
Ru3–N33	1.969(12)	Ru3–O31	1.991(9)
Ru3–O32	1.966(9)	Ru3–O35	1.868(6)
O31–C31	1.44(2)	C31–C32	1.52(2)
C32–N32	1.49(2)	N32–C35	1.38(2)
C35–C36	1.55(2)	C36–N33	1.36(2)
N33–C37	1.48(2)	C37–C40	1.45(3)
C40–O32	1.50(3)		
N31–Ru3–O32	111.3(7)	N31–Ru3–N33	110.0(7)
N31–Ru3–N32	111.6(7)	N31–Ru3–O31	109.1(6)
N31–Ru3–O35	174.5(6)	O35–Ru3–O32	64.6(4)
O35–Ru3–N33	73.2(5)	O35–Ru3–N32	72.8(4)
O35–Ru3–O31	68.1(4)	O32–Ru3–N33	79.6(4)
O32–Ru3–N32	136.9(5)	O32–Ru3–O31	90.0(4)
N33–Ru3–N32	81.9(5)	N33–Ru3–O31	140.6(5)
N32–Ru3–O31	80.3(4)		

ions and solvent water molecules: Na–O, 2.33–2.82(1) Å; (*iii*) hydrogen bonds from water molecules to oxygen atoms on two different anions: OH···O, 2.68–2.91(2) Å. In addition, there are three single hydrogen bonds from water molecules coordinated to ruthenium to nitrides on other anions; these are O25···N31 at $x-1$, y, $z-1$, 2.83(2) Å, O45···N51A at $x-1$, y, z, 2.47(2) Å, and O35···N51B at $-x$, $2+y$, $-z$, 2.55(2) Å. Finally, the exception to interaction *iii* is that solvent O4S donates only one hydrogen to an anion and another to O8S, 2.82(2) Å. In interaction *i* Na1 is chelated by the keto oxygen atoms of anion 2 and bonds to a keto oxygen of anion 1 and a coordinated oxygen of anion 4; its five-coordination is completed by a bond to water. Na2 is chelated by the keto oxygen atoms of anion 1 and bonds to a keto oxygen of anion 3; its six-coordination is completed by three bonds to water molecules. Na3 is chelated by the keto oxygen atoms of anion 5 and bonds to a keto oxygen of anion 4; its six-coordination is completed by three bonds to water molecules. Na4 bonds to a keto oxygen of anion 3 and has five bonds to water molecules while Na5 bonds to a coordinated oxygen atom of anion 3 and has five bonds to water molecules. A four-membered ring is formed by Na2 and Na4, both bonded to O2S and O3S.

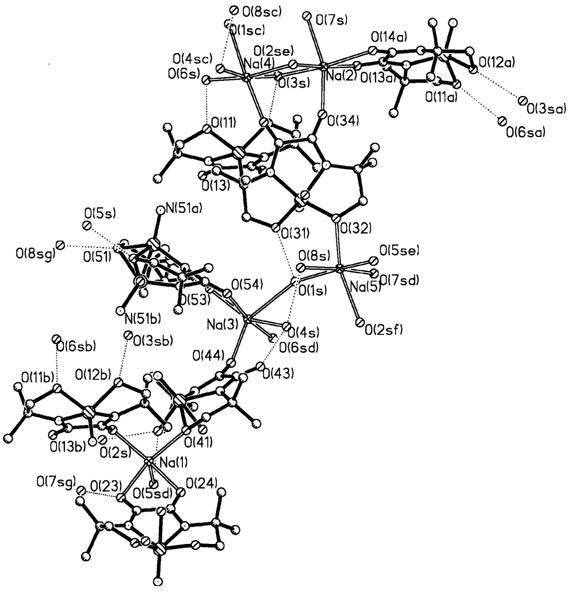
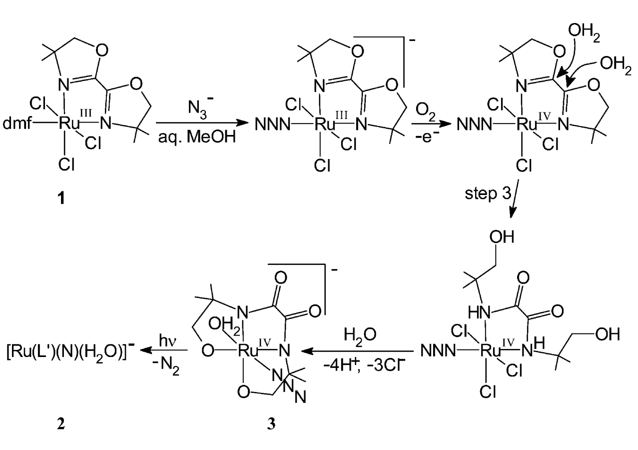


Fig. 2 View of the crystal structure of **2** approximately down the *b* axis. Na–O contacts are shown as open bonds and hydrogen bonded contacts as dotted lines. The equivalent positions are: (a) $1-x$, $\frac{1}{2}+y$, $1-z$; (b) $x-1$, y, $z-1$; (c) $x+1$, y, z; (d) $x-1$, y, z; (e) $-x$, $\frac{1}{2}+y$, $-z$; (f) $-1-x$, $\frac{1}{2}+y$, $-z$; (g) $-x$, $-\frac{1}{2}+y$, $-z$. Atoms N(51a) and N(51b) are disordered atoms with 75% and 25% occupancies, respectively.

In order to understand the mechanism of the reaction of azide with **1**, we have isolated an intermediate, **3**, from the acetonitrile extract by adding benzene dropwise to the solution. We have not been able to grow single crystals of **3** suitable for X-ray crystallography. The FTIR spectrum of **3**, however, shows very strong peaks due to coordinated azide (at 2053 cm^{-1})[10] and amide carbonyl (at 1667 cm^{-1}; *cf.* 1670 cm^{-1} in **2**) groups. Complex **3** has a room temperature magnetic moment corresponding to two unpaired electrons and displays a ^1H NMR spectrum very similar to that of **2**. From these physical data, together with molar conductance and elemental analyses (see Experimental), it is concluded that **3** is a Ru(IV) complex of the formulation $Na[Ru(L')(N_3)(H_2O)]\cdot 2CH_3OH\cdot 2H_2O$. The presence of two methanol molecules in **3** is confirmed by ^1H NMR. The structure of the anion $[Ru(L')(N_3)(H_2O)]^-$ is assumed to be essentially the same as that of $[Ru(L')(N)(H_2O)]^-$ with the azide group occupying the same position as the nitride, that is trans to the aquo ligand. We have found that **3** can only be converted into **2** by layering an acetonitrile solution of **3** over benzene for 3 weeks, thus providing convincing evidence of the intermediacy of **3** in the formation of **2**.

Complexes **2** and **3** have been studied by cyclic voltammetry but have been found to be electro-inactive in the potential range 1.8 to −1.8 V [*vs.* a saturated calomel electrode (SCE) in dmf at a platinum or glassy carbon electrode].

We have mentioned earlier that reaction (2) can be brought about either thermally or photolytically. In our case, generation of nitride from the coordinated azide is effected by the latter. That is, the conversion **3** → **2** or the generation of **2** from the acetonitrile extract obtained in the reaction of azide ion with **1** does not occur in the absence of light. A tentative mechanism for the overall reaction is proposed in Scheme 1. Substitution of the dmf ligand in **1** by azide in the first step leads to an anionic Ru(III) complex. The Ru(IV/III) couple in the neutral complex **1** in acetonitrile is 1.22 V *vs.* SCE.[9] The corresponding couple in the anionic complex $[Ru(L)(N_3)Cl_3]^-$ is expected to be lower, such that the complex can be oxidised by air (step 2), resulting in formation of the neutral Ru(IV) complex, $Ru(L)(N_3)Cl_3$. [To illustrate how a negative charge can lower a redox potential, we mention that substitution of pyrazole by its anion pyrazolate in the coordination sphere of Ru(II) decreases the Ru(III/II) potential by 0.44 V.[11] We also point out that the redox potential for the electrode process $O_2 + 4{\cdot}H^+ + 4{\cdot}e^- = 2{\cdot}H_2O$ is 0.99 V *vs.* SCE.[1b]]. The C–O bonds of the bisoxazoline moiety in $Ru(L)(N_3)Cl_3$ are hydrolysed, giving rise to $L'H_4$, which can then act as a tetradentate N_2O_2 donor chelate releasing four protons and resulting in the removal of two Cl^- ions. Exchange of a water for the third



Scheme 1

Cl^- ion yields the anion in **3**. The driving force behind the hydrolysis of L is that the amide nitrogen atoms can stabilise the high oxidation state Ru(IV) much better than could the donor atoms of a 1,4-diimine.

A number of Ru(VI) nitrido complexes are known in the literature.[4] These are prepared by reacting suitable ligands (usually containing amide nitrogens) with the preformed Ru(VI) nitrido complexes of the type $[Ru(N)Cl_5]^{2-}$. The Ru(VI)–nitride bonds in these complexes lie in the range 1.59–1.62 Å. To the best of our knowledge, no Ru(IV) azido complex is known so far and complex **3** is the first example. On the other hand, several azido complexes of Ru(III) have been described.[6,12] These complexes undergo spontaneous or thermal/light induced azide → metal electron transfer, yielding Ru(II) complexes. For example, $[Ru(NH_3)_5(N_3)]^{2+}$ spontaneously decomposes[6] to $[Ru(NH_3)_5(N_2)]^{2+}$ while $[Ru(bpy)_2(N_3)_2]^+$ (bpy = 2,2′-bipyridine) yields[12] $[Ru(bpy)_2(CH_3CN)(N_3)]^+$ in acetonitrile on heating or in the presence of light. Thus, our present studies add a new dimension to the nitrido chemistry of ruthenium.

Experimental

$Ru(L)(dmf)Cl_3$ (**1**) was synthesised as reported elsewhere.[9] Micro-analyses were performed on a Perkin–Elmer 2400II elemental analyser. Molar conductance was determined by a Systronics (India) direct reading conductivity meter (model 304). FTIR spectra (KBr disc) were recorded on a Nicolet Magna-IR spectrophotometer (Series II), UV-VIS spectra on a Shimadzu UV-160A spectrophotometer and ^1H NMR spectra (in DMSO-d_6) by a Brucker DPX300 spectrometer. Cyclic voltammetry was performed using an EG&G PARC electrochemical analysis system (model 250/5/0). Magnetic susceptibility was determined at room temperature by a PAR 155 vibrating sample magnetometer. The magnetometer was calibrated with $Hg[Co(SCN)_4]$ and the susceptibility data were corrected for diamagnetism using Pascal's constants. In the calculation of the magnetic moment of **3**, we have ignored the temperature-independent paramagnetism (TIP) of the Ru^{4+} ion.

Syntheses

$Na[Ru(L')(N)(H_2O)]\cdot 1.4H_2O$ (2). **1** (0.16 g, 0.33 mmol) was dissolved in 20 ml of methanol. To this yellow solution, 0.16 g (2.5 mmol) of NaN_3 dissolved in 3 ml of water was added dropwise. The resulting solution was stirred at room temperature for 8 h during which time the colour of the solution changed from yellow to deep red. The reaction mixture was stored in a desiccator over fused $CaCl_2$. The solid residue obtained after complete evaporation of the solvent was dissolved in a minimum volume of acetonitrile (20–25 ml typically required) and then filtered. The filtrate was layered over benzene. Yellow crystals of **2** suitable for X-ray crystallography were obtained after three weeks. Yield: 0.03 g (22%). Anal. found (calcd): C, 29.22 (29.31); H, 5.24 (5.12); N, 10.11 (10.26)%. FTIR ν/cm^{-1} (KBr): 1670 vs (C=O). Diamagnetic. $\Lambda_M/\Omega^{-1}\ cm^2\ mol^{-1}$ (CH_3OH): 68 (less than 1:1 electrolyte). UV/VIS λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) ($CH_3OH$): 251 (8400), 208 (14200). δ_H (300 MHz, DMSO-d_6, TMS): 1.27 (s, 6 H, methyl), 1.38 (s, 6 H, methyl), 4.01 (s, 4 H, methylene).

$Na[Ru(L')(N_3)(H_2O)]\cdot 2CH_3OH\cdot 2H_2O$ (3). To the acetonitrile extract obtained above in the synthesis of **2**, benzene was added dropwise until the solution became cloudy, at which point it was stored at 0 °C for 30 min, after which time a gummy precipitate was obtained. The solvent was decanted off and the precipitate was dried *in vacuo* over fused $CaCl_2$ to obtain **3** as a brown solid. Yield: 0.05 g (30%). Anal. found (calcd): C, 28.42 (28.11); H, 5.72 (5.90); N, 13.57 (13.66)%. FTIR ν/cm^{-1} (KBr): 2053 vs (N_3^-); 1667 vs (C=O). μ/μ_B: 2.94 (at 300 K). $\Lambda_M/\Omega^{-1}\ cm^2\ mol^{-1}$ (CH_3OH): 82 (1:1 electrolyte). UV/VIS λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$) ($CH_3OH$): 218 (15200), 247 (12100), 341 (2800). δ_H (300 MHz, DMSO-d_6, TMS): 1.28 (s, 6 H, methyl), 1.37 (s, 6 H, methyl), 3.47 (s, 6 H, methyl protons of methanol), 4.01 (s, 4 H, methylene).

Conversion of 3 to 2. **3** (0.05 g, 0.1 mmol) was dissolved in 25 ml of acetonitrile and the solution filtered. The yellow filtrate was layered over benzene. After three weeks, yellow crystals of **2** were obtained. Yield: 0.03 g (70%).

X-Ray crystallography

The 7496 independent reflections for **2** were collected on an automatic four-circle Nicolet R3mV diffractometer at 293(2) K using graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods (SHELXS-86[13]). The asymmetric unit contains four six-coordinate anionic complexes $[Ru(L')(N)(H_2O)]^-$, one five-coordinate anionic complex $[Ru(L')(N)]^-$, five sodium ions and eight lattice water molecules. One of the six coordinate anions is severely disordered, with two positions for the N–Ru–OH_2 unit related by an approximate twofold rotation about an axis running through the mid-point of the Ru5–O55 and C55–C56 bonds. The disorder over the two sites was first refined and then fixed at 75:25. The two positions for the ruthenium result in a second set of coordinates for the ligand L′. Only the nitrogen atoms N51 and N52 were sufficiently well-resolved that two sets of coordinates could be successfully refined, although very weak peaks in the electron density difference maps are apparent. In the disordered anion all the atoms were refined isotropically and hydrogen atoms were not included. For the other anions, the sodium and the solvent water non-hydrogen atoms were refined anisotropically (with the exception of C38, C39, C41 and C43, the anistropic refinement of which gave meaningless results). Hydrogen atoms were added in idealised positions for the ordered anions but no attempt was made to include the hydrogen atoms associated with the water molecules. Full matrix least-squares refinement (based on F^2; SHELXL-93[14]) gave $R_1 = 0.0609$, $wR_2 = 0.1597$ [7053 reflections, $I > 2\sigma(I)$] and $R_1 = 0.0660$, $wR_2 = 0.1697$ for 7488 absorption-corrected reflections and 841 parameters. The Flack parameter refined to 0.02(5), confirming the chirality. The largest peak in the final electron density map was 1.35 e $Å^{-3}$ [closest contact Ru(1)] and the largest hole −1.72 e $Å^{-3}$. The maximum shift/e.s.d. in the final cycle was 0.014.

CCDC reference number 205548. See http://www.rsc.org/suppdata/nj/b3/b301150j/ for crystallographic files in CIF or other electronic format.

Crystal data for 2. $C_{10}H_{20.8}N_3NaO_{6.4}Ru$: $M_w = 409.6$, monoclinic, space group $P2_1$, $a = 12.078(2)$, $b = 19.010(4)$, $c = 18.010(4)$ Å, $\beta = 97.77(3)°$, $U = 4097(1)$ $Å^3$, $Z = 10$, $D_c = 1.66\ g\ cm^{-3}$, $\mu = 1.0\ mm^{-1}$.

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