

X-Ray Crystal Structure of $[\text{Ru}_2\text{N}(\text{ethylenediamine})_5]\text{Cl}_5 \cdot \text{H}_2\text{O}$; a Novel Complex containing both Nitrido and Ethylenediamine Bridges

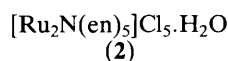
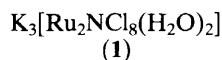
William P. Griffith,* Neil T. McManus, and Andrzej C. Skapski*

Chemical Crystallography and Inorganic Chemistry Laboratories, Imperial College, London SW7 2AY, U.K.

The title compound contains a short, symmetrical, slightly bent nitrido bridge, and the two ruthenium atoms are also spanned by an ethylenediamine bridge; ^{13}C n.m.r. data suggest that this structure is maintained in solution.

The complex $\text{K}_3[\text{Ru}_2\text{NCl}_8(\text{H}_2\text{O})_2]^1$ (**1**) undergoes a number of substitution reactions in aqueous solution.² We find that prolonged action of aqueous ethylenediamine (en) on (**1**) gives the title complex (**2**). We present here X-ray data which show this to be the first example of a μ -nitrido complex in which there is also a μ -en ligand, and it is the first structurally authenticated example of a complex containing an en ligand which has a co-bridging role.

The complex (**2**) was prepared by boiling a mixture of excess of aqueous en with (**1**), and the crystals were isolated as orange needles by addition of a little concentrated HCl.†



Crystal data for $\text{Ru}_2\text{C}_{10}\text{H}_{42}\text{Cl}_5\text{N}_{11}\text{O}$, orthorhombic, $a = 18.364(3)$, $b = 22.684(4)$, $c = 25.593(5)$ Å, $U = 10661$ Å³ (at

19°C), space group $Fddd$ and $Z = 16$. X-Ray diffraction data were collected on a Nicolet R3m/Eclipse S140 diffractometer system using an ω scan technique with graphite-monochromated $\text{Cu-K}\alpha$ radiation. A total of 1766 independent reflections were measured (to $\theta = 57^\circ$), of which 190 were 'unobserved.' The structure was solved by Patterson and

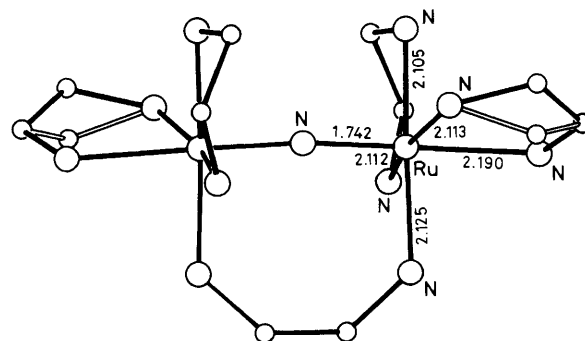


Figure 1. Structure of the $[\text{Ru}_2\text{N}(\text{en})_5]^{5+}$ cation. The open bonds indicate the conformational disorder which affects one of the independent chelating ligands. The crystallographic twofold axis which relates the two halves of the cation lies in the plane of paper.

† Satisfactory elemental analyses (C,H,N,Cl) were obtained.

Fourier methods, and least-squares refinement has now reached $R = 0.031$.[‡]

The binuclear $[\text{Ru}_2\text{N}(\text{en})_5]^{5+}$ cation is shown in Figure 1. It lies on a crystallographic twofold axis, which passes through the bridging nitrido nitrogen and through the mid-point of the bridging en ligand. Two chelating en ligands complete the approximately octahedral co-ordination about each metal atom.

The nitrido bridge is symmetrical [Ru–N, 1.742(1) Å, compared with 1.720(4) Å in (1)³], and is slightly bent with an Ru–N–Ru angle of 174.6(4)°. This bending is a consequence of the presence of the co-bridging en group. Another consequence of this strain is that, whereas the mean of three N(bridge)–Ru–N(equatorial) angles is 96.0°, consistent with the normal behaviour of ligands *cis* to a bridging nitrido ligand to subtend angles greater than 90°, the same angle formed by the bridge en nitrogen atom is 89.0(2)°.

The mean equatorial Ru–N(en) distance of 2.113 Å is significantly shorter than the *trans* Ru–N(en) distance of 2.190(4) Å, suggesting a *trans* weakening effect of the bridging nitride group.

The two groups of equatorial Ru–N(en) bonds are staggered when viewed down the Ru···Ru axis, with an average twist angle of *ca.* 38°. Given the multiple-bond character of the Ru–N–Ru system, an eclipsed conformation would have been preferred as in (1). This, however, is not possible because the

en ligand has to span a large Ru–N–Ru distance without being able to adopt the *anti* conformation usually found in binuclear complexes where en is the only bridge.⁴ Despite the staggered conformation in (2), the Ru–N–Ru system clearly retains considerable multiple-bond character, with the Ru–N (nitrido) distances being only *ca.* 0.02 Å longer than those in (1). The i.r. spectrum of the solid complex shows the asymmetric Ru–N–Ru stretch at 1048 cm⁻¹, compared with 1083 cm⁻¹ in (1), consistent with a very small decrease in bond strength.

The ¹³C{¹H} n.m.r. spectrum of the complex in aqueous solution consists of five sharp singlets of equal intensity (δ_c 58.2, 55.4, 54.7, 52.9, and 50.8 p.p.m. relative to Me₄Si), suggesting that the cation is non-fluxional and maintains its structure in solution at ambient temperature.

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[‡] Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.