(Ethylenediaminetetraacetato)nitrosylruthenium, An Efficient Oxygen-atom Transfer Agent†

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The complex [Ru(edta)(NO)] (edta = ethylenediaminetetraacetate) has been synthesised and characterised by physicochemical methods. An X-ray single-crystal analysis shows that the metal ion has an octahedral disposition with five-co-ordinated edta and NO^+ bound in a linear manner. The free carboxylic acid moiety is deprotonated to balance the charge of NO^+ in the neutral complex. The complex is an excellent oxygen-atom transfer agent towards hex-1-ene to form hexan-2-one and cyclohexene to form epoxide in a catalytic cycle with no need for a cocatalyst. The catalyst retains its activity over many turnovers.

Dioxygen activation and oxygen-atom transfer by metal complexes have attracted much attention due to their biological and industrial applications.[1–5] The oxygen-atom transfer reactions through a co-ordinated nitrosyl group and *via* the nitrosyl–nitro redox couple have assumed great significance.[6–10] Palladium(II) complexes were used as catalysts in the oxidation of terminal olefins and cyclooctene through a bimetallic catalyst consisting of Pd^{II}–NO + $CuCl_2$,[8] Co–NO + $PdCl_2$[9] and Rh–NO + $PdCl_2$.[10] In all these reactions the yield of the oxidised olefin was low with a small turnover number.[6] The complex $[Ru(NO)(PMe_3)_2(terpy)]^{3+}$ (terpy = 2,2′:6′,2″-terpyridine) was reported[11] to act as an O-atom transfer agent in the oxidation of olefins; $[Fe(NO)_3Cl_2\{P(NMe_2)_3O\}]$ and $[Fe(NO_3)Cl\{P(NMe_2)_3O\}_2]$ catalyse the oxidation of cyclohexene to allylic oxidation products.[12]

We have found that the Ru^{III}–edta–NO/Ru^{V}–edta–NO_2 redox couple (edta = ethylenediaminetetraacetate) acts as a potential O-atom donor for the oxidation of terminal olefins to ketones and cyclic olefins to epoxides. The system is monometallic and to our knowledge is the first to give a very high yield of ketones from terminal olefins. We report the synthesis and X-ray structural characterisation of (ethylenediaminetetraacetato)nitrosylruthenium [Ru(edta)(NO)] **1**.

Results and Discussion

Complex **1** is a non-electrolyte in dimethylformamide (dmf) solution. Its infrared spectrum contains a band at 1880 cm^{-1} assigned[13] to $\nu(NO^+)$, and a broad and strong band at 1660 cm^{-1} assigned to $\nu(CO_2^-)$ of co-ordinated carboxylate.[14] Complex **1** is paramagnetic, the μ_{eff} value at room temperature being 1.89 as expected for a low-spin d^5 system.[13] The EPR spectrum in the polycrystalline phase gave two signals corresponding to $g_{\parallel}$ 2.22 and $g_{\perp}$ 1.94 indicating axial compression.[15] The differential pulse polarogram and cyclic voltammogram of a solution of complex **1** in dmf under N_2 revealed the Ru^{3+}–Ru^{2+} couple at −0.211 V.

Crystal and Molecular Structure of Complex **1**.—Relevant crystallographic data for the complex are shown in Table 1, while Table 2 lists the final positional parameters and selected bond lengths and angles are shown in Table 3. These tables also carry information about the estimated standard deviations which are only slight underestimates because of the use of full-matrix least-squares refinement.

Table 1 Crystallographic data for complex **1**

Molecular formula	$C_{10}H_{12}N_3O_9Ru$
M	419.29
Space group	$P2_1/c$ (monoclinic)
Data collected	$+h, +k, \pm l$
T	295
a/Å	8.546(1)
b/Å	8.929(1)
c/Å	17.904(2)
β/°	98.37(1)
U/Å^3	1351.7(5)
μ/cm^{-1}	101.60
Transmission coefficient (%)	28.02–96.43
Z	4
D_c/g cm^{-3}	2.060
F(000)	836

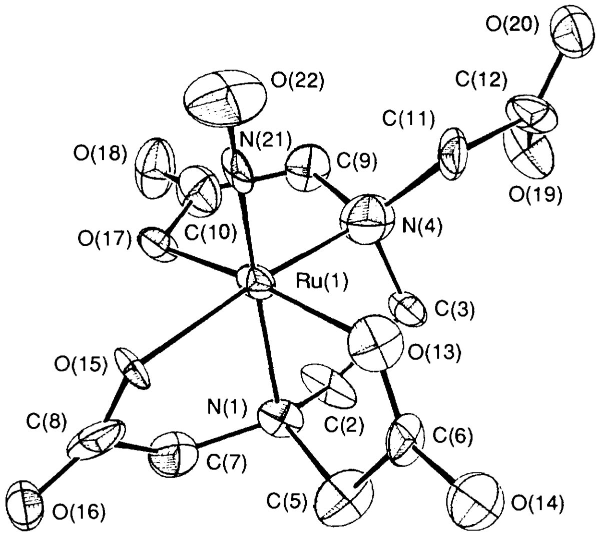

Fig. 1 An ORTEP view of [Ru(edta)(NO)] **1**

Fig. 1 shows an ORTEP[16] view of the molecule along with the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Positional parameters of non-hydrogen atoms and their estimated standard deviations for complex **1**

Atom	*x*	*y*	*z*
Ru	0.206 26(3)	0.832 63(3)	0.142 88(1)
O(13)	0.357 5(4)	0.851 7(4)	0.240 1(2)
O(14)	0.438 9(5)	0.733 8(7)	0.349 1(2)
O(15)	0.013 6(3)	0.861 9(3)	0.193 6(2)
O(16)	−0.196 7(4)	0.728 1(5)	0.223 4(2)
O(17)	0.060 1(3)	0.773 4(4)	0.048 5(2)
O(18)	0.059 6(5)	0.698 5(6)	−0.068 4(2)
O(19)	0.669 7(4)	0.648 6(4)	0.027 5(2)
O(20)	0.761 9(4)	0.888 7(6)	0.040 3(2)
O(22)	0.243 8(7)	1.147 8(5)	0.122 0(3)
N(1)	0.183 4(4)	0.615 3(4)	0.184 1(2)
N(4)	0.386 1(7)	0.749 0(7)	0.084 7(3)
N(21)	0.228 5(3)	1.021 2(4)	0.125 6(2)
C(2)	0.259 2(5)	0.513 1(7)	0.131 4(2)
C(3)	0.412 9(4)	0.590 4(5)	0.115 7(2)
C(5)	0.253 1(8)	0.599 4(7)	0.265 2(3)
C(6)	0.364 8(5)	0.732 7(5)	0.282 7(3)
C(7)	0.008 6(6)	0.599 6(8)	0.176 6(3)
C(8)	−0.077 0(8)	0.743 2(7)	0.195 5(3)
C(9)	0.310 6(6)	0.730 8(7)	0.004 2(2)
C(10)	0.131 8(6)	0.739 8(8)	−0.007 0(3)
C(11)	0.535 8(4)	0.836 0(7)	0.091 9(2)
C(12)	0.676 1(6)	0.782 0(6)	0.056 0(2)

Table 3 Selected bond distances (Å) and angles (°) with e.s.d.s in parentheses for complex **1**

Ru–O(13)	2.018(3)	Ru–N(1)	2.095(4)
Ru–O(15)	2.010(3)	Ru–N(4)	2.115(7)
Ru–O(17)	2.021(3)	Ru–N(21)	1.728(4)
O(13)–Ru–O(15)	93.7(1)	O(15)–Ru–N(21)	94.2(1)
O(13)–Ru–O(17)	169.7(1)	O(17)–Ru–N(1)	88.5(1)
O(13)–Ru–N(1)	81.7(1)	O(17)–Ru–N(4)	84.3(2)
O(13)–Ru–N(4)	92.0(2)	O(17)–Ru–N(21)	100.1(1)
O(13)–Ru–N(21)	89.9(1)	N(1)–Ru–N(4)	87.6(2)
O(15)–Ru–O(17)	88.0(2)	N(1)–Ru–N(21)	169.8(1)
O(15)–Ru–N(1)	80.6(1)	N(4)–Ru–N(21)	98.6(2)
O(15)–Ru–N(4)	166.0(2)		

numbering scheme. The neutral complex occurs as DL diastereomeric pairs, related by the centre of inversion of the space group $P2_1/c$. The ligand edta is pentadentate, with the free carboxylate arm deprotonated to balance the charge due to NO^+, which binds at the sixth position of the distorted octahedron of Ru^{III} [Ru–N–O 172.8(4)°] in a linear manner. The distortion in the octahedron is reflected in the range of *cis* and *trans* angles (81.7–98.6 and 166–169.7°, respectively). The lengths of the twelve edges of the octahedron vary from 2.655(3) to 2.973(3) Å, with an average of 2.898(3) Å. A comparison of these values with those of $[Ru(Hedta)(H_2O)]$ **2**[17] show that the distortion in the metal octahedron is slightly less in the case of complex **1**.

The complex [Ru(edta)(NO)] can be considered as a derivative of $[Ru(Hedta)(H_2O)]$ in which the water molecule has been replaced by an NO^+ ion. This substitution leads to a loss of hydrogen bonding and also a crowded environment around NO^+. As a consequence, one would expect some changes in the geometry, conformation and packing of this molecule compared to the aqua-complex **2**. The introduction of NO^+ in the place of water has produced a *trans* effect, which in turn results in an elongation of Ru–N(1) to 2.095(4) Å [*cf.* 2.035(2) Å in complex **2**]. The Ru–O(13) [2.018(3) Å] and Ru–O(15) bonds [2.010(3) Å], average 2.014(3) Å, are slightly but significantly longer than the value of 1.990(2) Å found in **2**. The difference between Ru–N(1) and the average of Ru–O(13) and Ru–O(15) in this complex is around 0.081(4) Å, much longer than that found for **2** and results from the *trans* effect on N(1). The Ru–N(4) bond length of 2.115(7) Å is not significantly different from that found for **2**, but Ru–O(17) 2.021(3) Å is significantly shorter than the value [2.062(2) Å] for **2**. An inspection of related structures of ruthenium aminopolycarboxylates shows that the length of the bond corresponding to Ru–O(17) can vary {for example 2.045(3) Å in $[Ru(Hpdta)(H_2O)]\cdot H_2O$[18] (pdta = isopropylenediaminetetraacetetate)} which must be attributed to the changes in geometry of the molecule and to the packing pattern in the crystal.

The C–O bonds of the co-ordinated edta groups follow the pattern found for other structures,[19] *i.e.* they are longer [1.305(6), 1.315(7), 1.276(7), average 1.297(7) Å] than the unco-ordinated O–C distances [1.262(6), 1.210(7), 1.235(7), average 1.236(7) Å]. There is an elongation of the double bond by 0.04 Å which is compensated by a contraction of the single bond by around 0.03 Å during complexation. The average of the N–C bond lengths is 1.500(7) Å, though the individual bonds vary from 1.487(6) to 1.523(7) Å. As in the case of complex **2**, the longest value pertains to the ethylenediamine collar and the shortest to the carbon carrying the free carboxylate group. The C–C bond lengths vary from 1.514(8) to 1.545(6) Å [average 1.529(6) Å] in agreement with those found in other structures.[19] Widening of the O–C–O angle in the carboxylate group occurs, which is compensated by a contraction in C–C–O. In complex **2** the distribution around the carboxyl moiety of the free carboxylate group is asymmetrical leading to a widening of the two angles, accompanied by a considerable contraction of one of the C–C–O angles, which can be attributed to the involvement of the free hydroxyl group in hydrogen bonding. In the NO^+ complex, however, this group is deprotonated leading to not widely differing C–O values, *i.e.* 1.293(7) and 1.253(8) Å, comparable to those found for the co-ordinated carboxyl groups in the molecule and widely different from the 1.324(4) and 1.204(4) Å found for the free carboxylic acid moiety. The asymmetry in the carboxyl group angles is similar to that found for the co-ordinated group and differs from that found in complex **2**.

Weakliem and Hoard[19a] based on calculations involving cumulative strain have made predictions on the conformations of the four glycinate rings in edta. Of the four possible rings involving glycinate groups in a hexadentate edta metal complex, the two which lie axial to the ethylenediamine will be less strained than those groups whose orientations are perpendicular to the collar. Rings R1 [Ru–N(1)–C(6)–C(5)–O(13)] and R2 [Ru–N(4)–C(5)–C(10)–O(17)] have root-mean-square (r.m.s.) deviations of 0.083(6) and 0.080(7) Å, respectively, while ring G [Ru–N(1)–C(7)–C(8)–O(15)] has a deviation of 0.212(5) Å. Summation of the five internal angles in R1 and R2 leads to 536.9 and 537.8°, respectively, which shows that R1 and R2 are equally strained. In the case of complex **2**, R1 is less strained than R2. Rings R1 and R2 can be described as shallow envelopes with N(1) displaced out of the mean plane Ru–C(6)–C(5)–O(13) by 0.277(6) Å (mean r.m.s. 0.028 Å) and with N(4) displaced by −0.279(7) Å (mean r.m.s. 0.025 Å) from the mean plane of Ru–C(9)–C(10)–O(17), respectively. Ring G is an envelope with N(4) displaced by −0.720 Å from the plane defined by Ru–C(7)–C(8)–O(15) (r.m.s. deviation 0.062 Å). A similar conformation for G is found in complex **2**. Ring E defining the ethylenediamine collar surprisingly has an envelope conformation, with C(2) displaced by 0.621 Å from the mean plane of Ru–N(1)–C(4)–C(3) [r.m.s. deviation 0.107(7) Å]. Though this ring is expected to adopt a half-chair conformation in edta metal complexes (a situation found in complex **2**), we believe that the conformation of this ring is flexible and depends on its environment, an observation in line with our findings on the structures of a number of derivatives of Hedta metal complexes, wherein this ring assumes an envelope conformation. In this case, we believe that the substitution of water by NO^+ is partially responsible for this change. The acetate groups are planar and have maximum deviations for any of the constituent atoms of 0.080(4), 0.078(5), 0.038(7) and 0.101(4) Å,

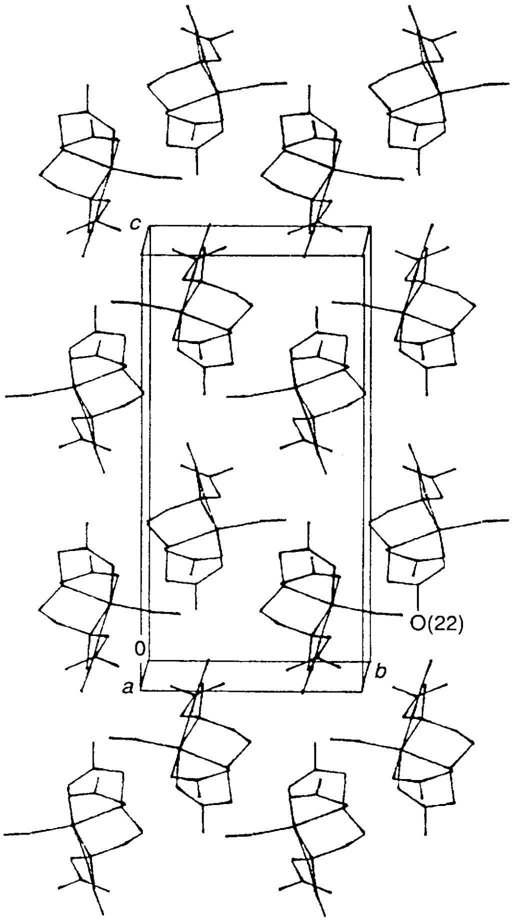

Fig. 2 Packing of the molecules viewed down the *a* axis

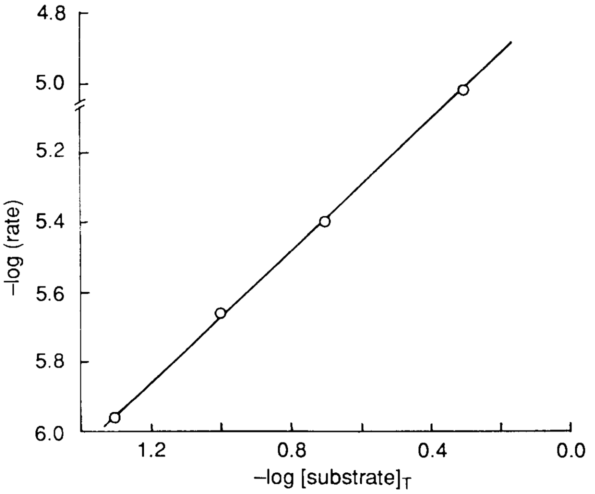

Fig. 3 Variation of the rate of oxidation of hex-1-ene by [Ru(edta)(NO)] as a function of hex-1-ene concentration

respectively for C(5)–C(6)–O(13)–O(14), C(7)–C(8)–O(18)–O(16), C(9)–C(10)–O(17)–O(18) and C(11)–C(12)–O(19)–O(20). The torsion angle N(1)–C(2)–C(3)–N(4) −55.2(2)° lies in the range found for other Ru–edta structures.[18,20,21]

The N–O distance of 1.141(6) Å is typical of a N≡O$^+$ contact; Ru–N(21)–O(22) is 172.8(4)°. The slight deviation from the ideal value of 180° must be attributed to the packing forces in the crystal structure. The dimensions of this Ru–N–O moiety compare well with those found in [Ru(OH)(NO$_2$)$_4$(NO)]$^{2-}$ (180°),[22,23] [RuCl$_5$(NO)]$^{2-}$ (176.7°)[24] and *trans*-[RuCl(NO)(py)]$^{2+}$ (py = pyridine) (174°).[22]

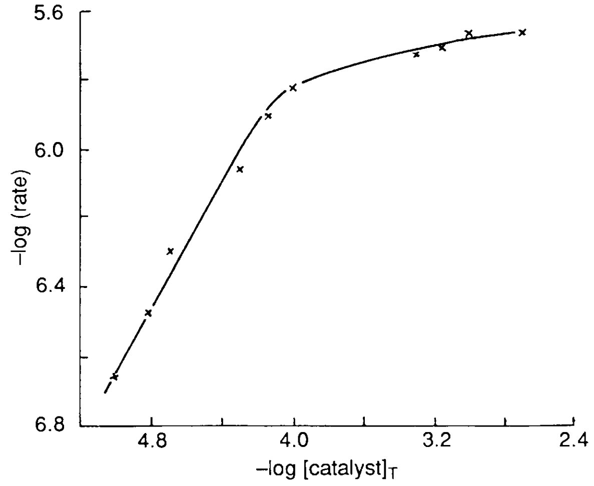

Fig. 4 Variation of the rate of oxidation of hex-1-ene by [Ru(edta)(NO)] as a function of catalyst concentration

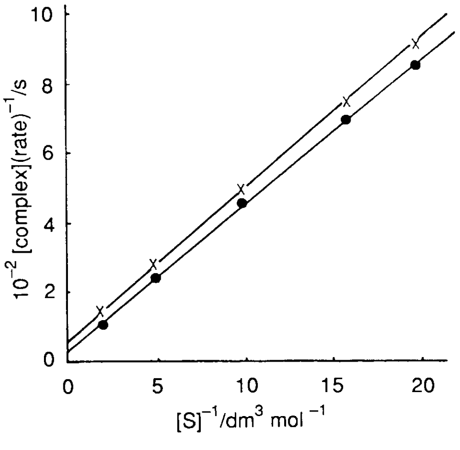

Fig. 5 Plot of [complex]$_T$/rate *vs.* [S]$^{-1}$ for the resolution of rate constant *k* at 35 °C. Substrates (S): ×, cyclohexene; ●, hex-1-ene

A view of the packing of the molecules in the unit cell is shown in Fig. 2. The structure is essentially held together by electrostatic interactions and the van der Waals forces. The NO$^+$ is encapsulated between the carboxyl groups of neighbouring edta moieties, O(22) being in contact with O(13) (3.346), O(14) (2.793), O(16) (2.943), O(18) (2.967), O(19) (3.404) and O(20) (2.918 Å).

Catalysis of the Oxidation of Hex-1-*ene and Cyclohexene by Complex* 1.—In the presence of molecular O$_2$, complex **1** catalyses the oxidation of hex-1-ene to hexan-2-one and cyclohexene to epoxide. This was studied in a manometric set up as described earlier.[25,26] The products were also estimated with respect to time by GC analysis. A plot of observed rate *vs.* concentration of hex-1-ene is linear (Fig. 3), indicating a first-order dependence of the rate on substrate concentration. The rate of the reaction was also found to be first order with respect to catalyst at lower catalyst concentration, tending towards saturation kinetics at higher concentration (Fig. 4). The rate of the reaction is half order with respect to molecular O$_2$ concentration. Similar results were obtained for the epoxidation of cyclohexene.[25] Based on the kinetic observations the mechanism in equations (1)–(3) is proposed for the oxidation of

$$2[\mathrm{Ru^{III}(edta)(NO)}] + \mathrm{O_2} \xrightleftharpoons{K_1} 2[\mathrm{Ru^{V}(edta)(NO_2)}] \quad (1)$$

$$[\mathrm{Ru^{V}(edta)(NO_2)}] + \mathrm{S} \xrightleftharpoons{K_2} [\mathrm{Ru^{V}(edta)(NO_2)(S)}] \quad (2)$$

$$[\mathrm{Ru^{V}(edta)(NO_2)(S)}] \xrightarrow{k} [\mathrm{Ru^{III}(edta)(NO)}] + \mathrm{SO} \quad (3)$$

the olefins (S) by molecular O_2 catalysed by **1**. The corresponding rate law takes the form (4) or (5). A plot of

$$\mathrm{Rate} = \frac{kK_1K_2[\mathrm{complex}]_\mathrm{T}[\mathrm{O_2}]^{\frac{1}{2}}[\mathrm{S}]}{1 + K_1[\mathrm{O_2}]^{\frac{1}{2}} + K_1K_2[\mathrm{O_2}]^{\frac{1}{2}}[\mathrm{S}]} \quad (4)$$

$$\frac{[\mathrm{complex}]_\mathrm{T}}{\mathrm{rate}} = \left(\frac{1}{kK_1K_2[\mathrm{O_2}]^{\frac{1}{2}}} + \frac{1}{kK_2}\right)\frac{1}{[\mathrm{S}]} + \frac{1}{k} \quad (5)$$

$[\mathrm{complex}]_\mathrm{T}$/rate *vs.* $[\mathrm{S}]^{-1}$ gave a straight line (Fig. 5) from which the values of k calculated from the intercept are 5.5×10^{-4} and 2.2×10^{-4} s^{-1} for the oxidation of hex-1-ene and cyclohexene, respectively at 30 °C. The value of K_1 at 30 °C is 3.45 dm^3 mol^{-1} and K_2 for hex-1-ene and cyclohexene are 0.92 and 1.57 dm^3 mol^{-1}, respectively. The turnover rates for the hex-1-ene and cyclohexene oxidations are 55 and 44 mol of product per mol of catalyst per hour.

A salient feature of the mechanism is the formation of the nitrito complex by O-atom addition to NO in reaction (1). The transfer of an O atom by complex **1** to the substrate was substantiated by ^{18}O studies. A mixture of $^{16}O_2$ and $^{18}O_2$ was passed through a reaction mixture containing complex **1** and the substrates hex-1-ene and cyclohexene. The oxidation products hexan-2-one and cyclohexene oxide were separated and their IR spectra recorded. The spectrum of hexan-2-one shows two absorption bands for ν(C=^{16}O) and ν(C=^{18}O) at 1710 and 1680 cm^{-1} respectively and for cyclohexene oxide corresponding bands at 1280 and 1250 cm^{-1}.

The salient feature of the catalytic system is the fact that it does not need any other metal ion as a cocatalyst for many turnovers of the product without loss or destruction of the catalyst.

Experimental

Physical Measurements.—Microanalysis of carbon, hydrogen and nitrogen was conducted by the Australian Mineral Development Laboratories (AMDEL), Australia. Conductivity measurement was done at 30 °C on a Digisum digital conductivity meter which was calibrated with 0.1 mol dm^{-3} KCl before use. Infrared spectra of complex **1** (4000–400 cm^{-1}) were recorded on a Shimadzu R435 spectrophotometer for a KBr pellet and solution. The EPR spectrum of **1** was recorded on a Bruker ESP 300 spectrophotometer, in the X band between 9 and 10 GHz using diphenylpicrylhydrazyl as standard.

The electrochemical measurements were carried out with a Princeton Applied Research (PAR) electrochemical instrument equipped with a precision X-Y recorder. A PAR 303 SMDE assembly provided with a dropping mercury electrode/hanging mercury drop electrode working electrode and a platinum wire (diameter 0.5 mm) electrode was used. All potentials were measured against a Ag–AgCl reference electrode at 25 °C. A medium-sized drop (2.75 mg) was used with an open circuit and a drop time of 2 s. The magnetic susceptibility was measured by the Evans' method.[27]

Synthesis of [Ru(edta)(NO)].—The complex K[Ru(Hedta)-Cl]·$2H_2O$ (0.5 g, 1 mmol) prepared by the reported procedure[14] was dissolved in water–ethanol (1:1) (15 cm^3) and flushed with nitrogen for 15 min. An aqueous solution (15 cm^3) of NOCl (3 mmol) was added slowly to the above solution and stirred for 6 h. This resulted in the formation of dark brown crystals of complex **1**, and its composition checked by elemental analysis.

Crystallography.—Dark brown crystals of the complex **1** were obtained by slow evaporation of an aqueous solution at room temperature. One such crystal of dimensions 0.16 × 0.14 × 0.36 mm was used for preliminary investigations and intensity data collection. Accurate cell dimensions were obtained using 25 arbitrarily chosen higher-order reflections between 2θ 25 and 60° (Cu-Kα). Intensity data were collected using graphite-monochromated Cu-Kα radiation (λ = 1.5418 Å) in the 2θ range of 4–110°. The stability and orientation of the crystal during the entire period of data collection was monitored by measuring two sets of three control reflections at regular intervals. The data were corrected for absorption by the empirical method of North *et al.*,[28] after correction for the Lorentz and polarisation factors. Of the 2157 independent reflections, 1464 had $I \geqslant 3\sigma(I)$ and were considered as observed.

Structure solution and refinement. The structure was solved by the heavy-atom method. An origin-removed sharpened three-dimensional Patterson synthesis gave the locations of the ruthenium atoms, which were subjected to three cycles of isotropic full-matrix least-squares methods. The resulting difference map gave the positions of all the non-hydrogen atoms. Hydrogen atoms were generated either by using stereochemical constraints or from the difference map constructed after a complete convergence by an anisotropic refinement and were given thermal parameters based on the non-hydrogen atoms to which they are attached. A full-matrix least-squares refinement in which the non-hydrogen atoms were refined anisotropically, while keeping the hydrogens fixed, resulted in convergence at an R 0.026 (R' = 0.027); a weighting scheme $w = 1.0$ for $F_o < 350$ and $w = (350/F_o) \times 2$ for $F_o > 350$, with a Dunitz–Seiler factor[29] was employed. The shift-to-error ratio in the final cycle for the non-hydrogen atoms was less than 0.01:1 and the refinement was considered to be complete. The Fourier difference map at this stage had ripples of maximum density of 0.39 e $Å^{-3}$. Scattering factors for ruthenium, oxygen, nitrogen and carbon were from ref. 30 while those for the hydrogens were from Stewart *et al.*[31] All the crystallographic computations were carried out using the SDP package of programs[32] available for the PDP-11/73 system.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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