The Application of *X*-Ray Photoelectron Spectroscopy to the Determination of the Structure of a Deprotonated Ethylenediamine Ruthenium Complex

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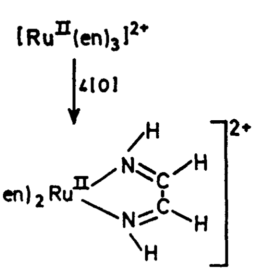
Summary A deprotonated ethylenediamine ruthenium complex, previously reported to be an Ru^{VI}–amide system, has been shown by *X*-ray photoelectron spectroscopy in conjunction with its diamagnetism, to be a ruthenium(II) complex, and shown by n.m.r. spectroscopy to contain an α-di-imine chelate ring.

BECAUSE of the recent communication[1] on the activation of amines by co-ordination to Ru^{II} and reference made therein to the oxidation[2] of $[Ru(en)_3]^{2+}$, we felt that we should report some of our preliminary observations on this $[Ru(en)_3]^{2+}$ oxidation. The product of oxidation of $[Ru^{II}(en)_3]^{2+}$ or $[Ru^{III}(en)_3]^{3+}$ by air or I_2 was recently characterized[2] as $[Ru(en_3 - 4H)]I_2$. This product was identified as a complex of Ru^{VI}, a conclusion based on the consumption of 4 equivalents of oxidant by $[Ru^{II}(en)_3]^{2+}$ and 3 equivalents of oxidant by $[Ru^{III}(en)_3]^{3+}$ in its production. Deprotonation of amines co-ordinated to metals in high oxidation states is common, and this was suggested to account for the +2 charge found on the cation.



(I)

We have shown by *X*-ray photoelectron spectroscopy that the product is an Ru^{II} complex. Oxidation of the ligand has occurred, to give an α-di-imine chelate ring (equation 1) as shown by n.m.r. spectroscopy.

X-Ray photoelectron spectra, obtained with an AEI ES 100B spectrometer, of a series of ruthenium compounds showed an increase in the binding energy of the Ru $3d^{5/2}$ electron with increasing formal oxidation state, as expected (see Table). The values in the Table have not been corrected for Madelung energies. It should be noted that the signs of the Madelung energy correction terms are opposite for anionic and cationic sites. Hence the binding energy expected for an Ru^{VI} atom in a cationic site similar to the other ruthenium complexes reported would be considerably larger than that reported for $Ba[RuO_4]$. From the Table, it is clear that the compound produced by oxidation of $[Ru(en)_3]ZnCl_4$ is not an Ru^{VI} complex. The binding energy found for the Ru atom is between that found for typical Ru^{II} and Ru^{III} complexes, and the diamagnetism of the complex establishes it as an Ru^{II} species

TABLE

Formal oxidation state	Compound	Binding energy Ru $3d^{5/2}$, ev ±0.5 ev[a]	Line width (FWHM), ev
Ru^0	Ru metal	279	—
Ru^{II}	$[Ru(NH_3)_6]I_2$	279.8[b]	1.4
	$[Ru(en)_3]ZnCl_4$	280.4[c]	1.4
Ru^{III}	$[Ru(NH_3)_6](BF_4)_3$	282.2[b]	2.0
Ru^{VI}	$Ba[RuO_4]$	284.4[d]	—
Ru(?)	$[Ru(en_3 - 4H)]I_2$	281.3[c]	1.5

[a] The values have not been corrected for Madelung energies.

[b] Energy reference is C 1*s* of graphite whose binding energy is taken to be 284.0 ev.[3]

[c] Energy reference is C 1*s* of ethylenediamine in the compound whose binding energy is taken to be 285.7 ev.[4]

[d] Obtained from the Ru $3d^{3/2}$ peak position and the known Ru $3d^{3/2}$–Ru $3d^{5/2}$ separation.

Oxidation of the ligand rather than the metal atom has clearly taken place.

The N 1*s* ESCA spectrum of $[Ru(en_3 - 4H)]I_2$ gave two peaks, on deconvolution, with electron binding energies of 399·2 (intensity 2) and 397·9 ev (intensity 1).† The larger peak is at the same energy as that for $[Ru(en)_3]ZnCl_4$ (399·2 ev), and can be assigned to the four amine nitrogens, whereas the smaller peak can be assigned to the two imine nitrogens (see below). This N 1*s* ESCA spectrum is not consistent with the earlier formulation,[2] where the larger peak (for the four amide nitrogens) should have a *lower* binding energy than the smaller peak for the two amine nitrogens.

The i.r. spectrum of the complex shows no bands that could be attributed to a co-ordinated nitrile (in the region 2300—2150 cm^{-1}) or to CN^- (2040 cm^{-1}) as found[1] in the air oxidation of monodentate amines attached to Ru^{II}. The i.r. spectrum does show new bands, as compared with $[Ru^{II}(en)_3]ZnCl_4$, at 1199 and 837 cm^{-1} as well as some complex changes in the 1600—1300 cm^{-1} region.

The n.m.r. spectrum (60 MHz) of the complex in D_2O shows the expected broad CH_2 absorption at δ 2·6, and also a sharp singlet at δ 8·8, with relative intensities 4 : 1. The low-field absorption is characteristic of imine protons $(=C\text{–}H)$[5,6] and the absence of any splitting of this peak, compared with that found[5] for the $H_2\overline{NCH_2CH{=}NH\text{–}M}$ ring in similar compounds, shows the presence of an α-di-imine ring ($\overline{NH{=}CH\text{–}CH{=}NH\text{–}M}$), where the two imine C–H protons are equivalent. The protons on the nitrogen atoms exhibit broad peaks which have not been assigned.

The i.r. bands at 1199 and 837 cm^{-1} could be assigned to the $\delta(H\text{–}N{=})$ and $\delta(H\text{–}C{=})$ vibrational modes respectively which have previously been found in these regions for this type of compound.[7] The expected $\nu_{C=N}$ mode near 1580 cm^{-1} cannot readily be identified because of the strong bands already present in this region.

The activation of a saturated ligand towards oxidation on co-ordination to Ru has previously been observed only for monodentate amines,[1] where co-ordinated nitriles or CN^- were among the products. Oxidation of co-ordinated ethylenediamine to an imine by Cl_2 in a Pt^{IV} complex has also been reported.[7] The production of a co-ordinated nitrile in a five-membered ring is clearly unlikely for steric reasons in this case, and the oxidation takes a different course. It is interesting to note that $[Ru^{III}(en)_3]^{3+}$ also oxidizes to give this same product, a process in which reduction of the metal ion is concomitant with oxidation of the ligand. Similar redox reactions have also been noted for similar Fe^{III} complexes.[8]

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† The digital deconvolution was made assuming two contributing gaussian peaks each with the FWHM linewidth of 1·8 ev observed for N 1*s* in the ammine and ethylenediamine ruthenium complexes listed in the Table. Separation and relative peak heights were adjusted to obtain the best fit.

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