Synthesis and X-Ray Structural Study of a Novel Ruthenium(III)–Ethylenediaminetetraacetate Complex. The First Compound showing an *Unusual* Coordination Site for a Carboxylic (Glycine) Group

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Reaction of hydrated ruthenium trichloride in HCl and ethylenediaminetetraacetic acid (H_4edta) gives the antitumour complex [Ru(H_3edta)Cl_2]·$4H_2O$ whose X-ray structure shows the first example of a stable Ru–O=COHR (glycine) bond; this type of linking has been confirmed by IR and X-ray photoelectron spectroscopy.

Although the preparation[1–7] and properties[8–14] of ruthenium–ethylenediaminetetraaceto complexes have been the subject of numerous studies, there is no report on the structure of these compounds in the solid state. We report here the first crystallographic structure determination of a ruthenium(III)–edta complex,[1–14] one example of a recently investigated new group of promising anticancer compounds.[15] The most salient feature of the structure is the presence of one coordinated glycinate arm from edta through the oxygen atom of the C=O group, while the carboxylic oxygen atom remains protonated. The complex *cis*-dichloro[ethylenediaminetetraacetato(1−)] ruthenium(III) tetrahydrate **1** was prepared by a modification of the hydrothermal synthesis reported by Saito *et al.*[5]†

The molecular structure obtained by X-ray analysis is shown in Fig. 1.‡ The ruthenium(III) ion is coordinated in the equatorial plane by two nitrogen atoms from the tetradentate edta ligand and two chlorine atoms *cis* to each other. The remaining *trans* axial position are occupied by two oxygen atoms from edta glycinate groups. The ethylene group of the edta ligand adopts a distorted *gauche* structure but the geometry of the molecule is almost perfectly octahedral, showing similar distances Ru–X (X = N, Cl, O). The central core of the molecule is shown in Fig. 2.

The most striking consequence of the coordination of the carbonyl O(3) atom is the substantial lengthening of the O(3)–C(1C) distance (1.30 Å) as result of significant π back donation from metal to oxygen. Indeed, the average C=O distance in the free carboxylic groups is 1.21 Å [O(2)–C(1A) 1.20 and O(5)–C(2A) 1.22 Å], while the O(7)–C(2C) length (coordinated carboxylate group, is only 1.25 Å. Other C=O bond lengths (glycinate group) for related metal–edta complexes are in the range 1.23–1.25 Å.[17] All these data strongly suggest the existence of the bonding ruthenium(III)–O(3) (carbonyl). The observation of a strong IR band at 1950 cm^{-1} may be due to this type of bonding.[11]

X-Ray photoelectron spectroscopy (XPS) confirmed the above assumption. A strong band at a binding energy of 532.0 eV may be accounted for by the three carboxylic groups *ca.* 9.1% b.w. of protonated oxygen) while another small and broad peak at 533.5 eV arises from the coordinated carbonyl-type oxygen atom.

With the exception of the free carboxylic group O(6)–H(6), which is not involved in hydrogen bonding, all other carboxylate groups are associated with water molecules; while O(4) and O(7) atoms from opposite coordinated axial glycinate arms are bonded to the same water molecule oxygen O(9), two other water molecule atoms are associated with the complex in different fashions: O(10) and O(12) water atoms interact with O(1) and Cl(2), respectively. Finally, a fourth water molecule, O(11), is also associated with O(9) through hydrogen bonding.

The isolated complex is extremely soluble in water, stable to air at room temperature and shows paramagnetic behaviour, with a magnetic moment ranging between 1.78 μ_B (298 K) and

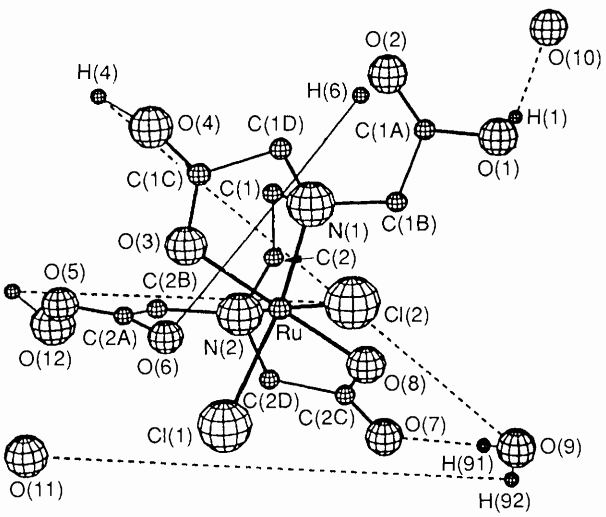

Fig. 1 Molecular structure of **1** showing the crystallographic atomic numbering scheme[16d] and the water of hydration. Important bond distances (Å) and angles (°): Ru–Cl(1) 2.372(2), Ru–Cl(2) 2.345(2), Ru–N(1) 2.115(5), Ru–N(2) 2.122(5), Ru–O(3) 2.030(4), Ru–O(8) 2.047(4), Cl(1)–Ru–Cl(2) 90.9(6), Cl(1)–Ru–N(2) 92.9(1), N(1)–Ru–N(2) 84.7(2), Cl(2)–Ru–N(1) 92.5(1), O(3)–Ru–O(8) 176.0(2). Hydrogen bonding interactions, some of which involve adjacent molecules, are indicated by dashed lines.

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† To a solution of $RuCl_3 \cdot 3H_2O$ (0.5 g) in HCl (100 ml; 0.1 mol dm^{-3}) solid H_4edta (0.585 g; Ru : edta, 1 : 1.2) was added, and the mixture was stirred for 2 h at 70 °C. The colour changed from deep red–purple to pale brown. The solution was filtered at room temperature, and slow evaporation gave yellow–orange prismatic crystals suitable for X-ray analysis. Satisfactory elemental analyses were obtained.

‡ *Crystal data* for **1**: $C_{10}H_{15}N_2O_8Ru \cdot 4H_2O$, M = 535.27, monoclinic, space group $P2_1/c$, a = 7.912(6), b = 14.235(2), c = 17.025(3) Å, β = 92.79(2)°; U = 1915(2) Å^3, Z = 4, D_c = 1.86 g cm^{-3}, $F(000)$ = 1084, μ = 11.4 cm^{-1}, Mo-Kα radiation (λ = 0.71069 Å), 4171 unique reflections measured with an Enraf-Nonius CAD4 diffractometer. Unit cell constants were refined from least-squares refinement of the setting angles of 25 reflections. There was 1% intensity variation of three standard reflections monitored periodically. Intensities were corrected for Lorentz and polarization factors. Scattering factors for neutral atoms and anomalous dispersion corrections for Ru and Cl were taken from ref. 16*a*. The structure was solved from a three-dimensional Patterson map and Fourier synthesis which allowed the location of all atoms other than hydrogen. An empirical absorption correction[16b] was applied at the end of the isotropic refinement. Anisotropic full-matrix least-squares refinement with unit weights led to R = 0.048. No trend in ΔF *vs.* F_o or sin θ/λ was observed. A difference synthesis calculated with those reflections having sin $\theta/\lambda < 0.5$ Å^{-1} showed all atoms as the highest peaks. Refinement with a fixed thermal parameter for H atoms, led to final values of R = 0.042 and R_w = 0.050. Most of the calculations were carried out with X-RAY 80.[16c] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

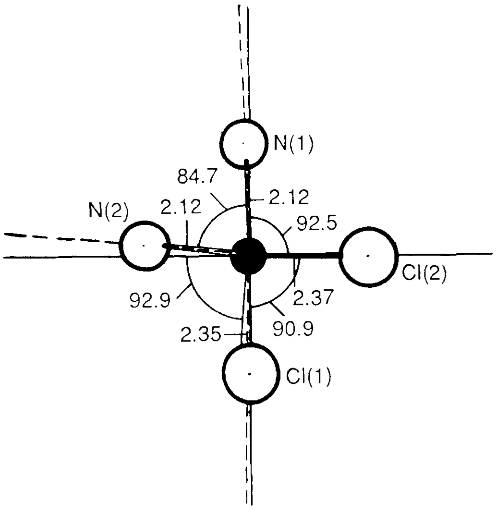

Fig. 2 Core O(3)–O(8) projection and labelling of the coordinated equatorial atoms of complex **1**, with distances in Å and angles in degrees

1.89 μ_B (80 K), which is as expected for one unpaired electron spin. These and other data[18] indicate an oxidation state of +3 for ruthenium, with a low-spin $4d^5$ configuration.§

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§ Potentiometric and electronic measurements are in agreement with formula **1**.