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Synthesis, structures and speciation studies of ruthenium(III) hydroxamate/hydroximato complexes. Crystal and molecular structure of hydrated [Ru(H_2edta)(2-methoxyphenylhydroxamate)], the first structurally characterised ruthenium(III)–hydroxamate complex

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Reaction of K[Ru(Hedta)Cl]·1.5H_2O with various phenylhydroxamic acids, R-PhaH, in aqueous solution affords the hydroxamate complexes [Ru(H_2edta)(R-Pha)]·$x$$H_2O$, the crystal and molecular structure of one of which *i.e.* hydrated [Ru(H_2edta)(2-OMe-Pha)], where 2-OMe-Pha = 2-methoxyphenylhydroxamate, has been determined. In this complex, the first reported structure of a Ru(III)–hydroxamate, the carboxylato groups of the tetradentate H_2edta are *trans* to each other and the amino nitrogen and hydroxamate oxygen donor atoms are roughly coplanar. Relevant bond lengths (Å) are: Ru–O(carboxylato) 2.016(4) and 2.044(3), Ru–O(hydroxamato O^-) 1.964(4), Ru–O (hydroxamato CO) 2.019(4), Ru–N 2.060(4) and 2.156(4). Addition of R-PhaH to an aqueous solution of K[Ru(Hedta)Cl]·1.5H_2O resulted in $[Ru(edta)(R\text{-}Pha)]^{2-}$ as the major species at pH 4–7. At higher pH the hydroxamate NH groups in these complexes undergo deprotonation to give the hydroximato complexes $[Ru(edta)(R\text{-}PhaH_{-1})]^{3-}$ as the major species at pH 7–11. This deprotonation, which has previously been reported in only a very small number of cases for mononuclear complexes, is accompanied by marked shifts to longer wavelengths in the ligand to metal charge transfer bands. At pH > 10 hydrolysis to give $[Ru(edta)(R\text{-}PhaH_{-1})(OH)]^{4-}$ in which an edta carboxylato group has been replaced by hydroxide ion is observed. Formation constants for the various species in solution are reported. The affinity of Pha for $[Ru(edta)(H_2O)]^-$ (hexacoordinated) is much greater than for $[Fe(edta)(H_2O)]^-$ (heptacoordinated) but this is largely due to differences in charge and coordination numbers of the immediate metal ion environments rather than intrinsic affinity differences between Ru(III) and Fe(III) for hydroxamate ligands.

Introduction

Hydroxamic acids are a family of weak organic acids of general formula, RC(O)NHOH and are found naturally in microbial siderophores where their chelating ability is utilised in the uptake of iron.[1] Hydroxamic acids are also inhibitors of enzymes such as peroxidases,[2] ureases,[3] and matrix metalloproteinases,[4] and can act as hypotensive,[5] antibacterial, anticancer, antibiotic and antifungal agents.[6] We have recently shown that hydroxamic acids are nitric oxide donors by their ability to react with ruthenium(III) complexes forming ruthenium(II) nitrosyls and physiologically to cause vascular relaxation of rat aorta by activation of the haem enzyme guanylate cyclase.[7] Furthermore acetylated hydroxamic acids act as aspirin analogues by inhibition of prostaglandin-H-synthase.[8] The versatile biological activity of hydroxamic acids is due to their strong metal ion chelating ability, their NO-releasing properties, their ability when ionised to form salt linkages in their complexes with proteins, or when unionised to engage in key hydrogen bonding interactions and to provide sites for acylation reactions.

The proposed mechanism of nitrosyl abstraction from hydroxamic acids by ruthenium(III) involves initial formation of ruthenium(III)–hydroxamate complexes. In view of the abundance of iron(III)–hydroxamate complexes which have been reported it is surprising that no ruthenium(III)–hydroxamate complexes have been structurally characterised to date. We report herein the synthesis of some such complexes by reaction of K[Ru(Hedta)Cl]·1.5H_2O with various hydroxamic acids and the X-ray structure of hydrated [Ru(H_2edta)(2-OMe-Pha)], the first ruthenium(III)–hydroxamate complex to be structurally characterised. We also report on the speciation of these systems in aqueous solution and on their deprotonation in weakly alkaline solution to give a family of Ru(III)–hydroximato complexes, previously reported in very few cases for mononuclear hydroxamate complexes. We also address the question of relative affinities of ruthenium(III) and iron(III) towards hydroxamate ligands.

Experimental

Materials

Acetohydroxamic acid (Acha), phenylhydroxamic acid (Pha), salicylhydroxamic acid (2-OH-Pha), methyl-2-methoxybenzoate, methyl-4-methoxybenzoate, methyl-2-nitrobenzoate, methyl-4-nitrobenzoate, methyl-2-chlorobenzoate, methyl-4-chlorobenzoate, methyl-4-methoxysalicylate, *o*-toluic acid, *p*-toluic acid and 4-hydroxybenzoic acid were purchased from Aldrich.

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Syntheses

Hydroxamic acids. 2-Methoxyphenylhydroxamic acid (2-OMe-Pha), 4-methoxyphenylhydroxamic acid (4-OMe-Pha), 2-nitrophenylhydroxamic acid (2-NO_2-Pha), 4-nitrophenylhydroxamic acid (4-NO_2-Pha) 2-chlorophenylhydroxamic acid (2-Cl-Pha), 4-chlorophenylhydroxamic acid (4-Cl-Pha), 2-methylphenylhydroxamic acid (2-Me-Pha), 4-methylphenylhydroxamic acid (4-Me-Pha), 4-hydroxyphenylhydroxamic acid (4-OH-Pha) and 4-methoxysalicylhydroxamic acid (2-OH,4-OMe-Pha) were synthesised according to literature methods,[9] by reaction of hydroxylamine with the corresponding methyl esters which were either purchased or synthesised from the parent acids.[10] Satisfactory microanalysis, ^{1}H NMR and IR spectra were obtained for all compounds.

K[Ru(Hedta)Cl]·1.5H_2O. This was prepared by modification of a literature method,[11] as follows. A solution of $RuCl_3.xH_2O$ (3 g, 14.5 mmol) and Na_2H_2edta·2H_2O (5.4 g, 14.5 mmol) in HCl (250 cm^{-3}, 0.1 mol dm^{-3}) was refluxed for 3 h or until the colour changed from dark brown to green. The black ruthenium oxide, which precipitated, was removed by filtration and KCl (1.1 g, 14.5 mmol) was added to the filtrate. The resulting solution was stirred for 1 h and the solvent was removed in vacuo. The residual solid was dissolved in minimum hot water, cooled and ethanol (~250 ml) was added to give a yellow product. Yield 4.2 g, 9.1 mmol, 63%. IR bands at 3452, 2940 (broad), 1726 (sharp), 1632 (strong, broad) cm^{-1}. Found: C, 24.19; H, 2.69; N, 5.55; K 8.11; Cl, 7.27. Ru $C_{10}H_{16}N_2O_{9.5}$KCl requires C, 24.42; H, 3.28; N, 5.70; K, 7.95; Cl, 7.21%.

[Ru(H_2edta)(2-OMe-Pha)]·2H_2O. An aqueous solution (30 ml) of 2-OMe-Pha (167 mg, 1 mmol) was added to an aqueous solution (15 ml) of K[Ru(Hedta)Cl]·1.5H_2O (500 mg, 1 mmol) and the resulting solution was stirred for 15 min and left to stand overnight in a refrigerator during which a red precipitate was obtained. This was filtered and dried over P_2O_5. Yield 350 mg, 0.6 mmol, 61%. IR bands 3475, 3356, 2947, 1730, 1652, 1605 cm^{-1}. Microanalysis: found C, 36.69; H, 4.04; N, 7.02. $RuC_{18}H_{26}N_3O_{13}$ requires C, 36.43; H, 4.42; N, 7.08%. The complex was found to have a μ_{eff} = 1.57 μ_B at RT consistent with a paramagnetic Ru^{III} metal centre. Single needle-shaped crystals suitable for X-ray studies were obtained by slow evaporation of a saturated solution of the complex in aqueous methanol (50 : 50).

The following ruthenium(III)–hydroxamates were synthesised by the above method. However in all cases the reaction solutions were concentrated from 45 to 15 ml *in vacuo* before being left overnight in a refrigerator.

[Ru(H_2edta)(4-OMe-Pha)]·2H_2O. Yield 57%. IR bands 3452, 2985, 1730, 1632, 1609 cm^{-1}. Microanalysis: found C, 36.34; H, 4.05; N 6.72. $RuC_{18}H_{26}N_3O_{13}$ requires C, 36.43; H, 4.42; N, 7.08%.

[Ru(H_2edta)(Pha)]·2H_2O. Yield 52%. IR bands 3437, 3210, 2989, 1730, 1617 cm^{-1}. Microanalysis: found C, 36.52; H, 4.11; N 7.15. $RuC_{17}H_{24}N_3O_{12}$ requires C, 36.24; H, 4.29; N, 7.46%.

[Ru(H_2edta)(4-NO_2-Pha)]·4H_2O. Yield 42%. IR bands 3429, 3180, 2950, 1732, 1641 cm^{-1}. Microanalysis: found C, 31.71; H, 3.91; N, 8.71. $RuC_{17}H_{27}N_4O_{16}$ requires C, 31.68; H, 4.22; N, 8.69%.

[Ru(H_2edta)(4-Me-Pha)]·1.5H_2O. Yield 58%. IR bands 3450, 3264, 2971, 1730, 1647 cm^{-1}. Microanalysis: found C, 38.05; H, 4.01; N 7.05. $RuC_{18}H_{25}N_3O_{11.5}$ requires C, 38.03; H, 4.43; N, 7.39%.

[Ru(H_2edta)(2-OH-Pha)]·2.5H_2O. Yield 52%. IR bands 3429, 3316, 2948, 1731, 1655, 1598 cm^{-1}. Microanalysis: found C, 34.40; H, 3.84; N 6.96. $RuC_{17}H_{25}N_3O_{13.5}$ requires C, 34.70; H, 4.28; N, 7.14%.

[Ru(H_2edta)(4-OH-Pha)]·2.5H_2O. Yield 51%. IR bands 3426, 3226, 3034, 1729, 1646, 1601 cm^{-1}. Microanalysis: found C, 34.58; H, 3.82; N, 6.82. $RuC_{17}H_{25}N_3O_{13.5}$ requires C, 34.70; H, 4.28; N, 7.14%.

[Ru(H_2edta)(2-OH-4-OMe-Pha)]·2H_2O. Yield 47%. IR bands 3480, 3285, 2984, 1730, 1645, 1611 cm^{-1}. Microanalysis: found C, 35.89; H, 3.92; N 6.58. $RuC_{18}H_{26}N_3O_{14}$ requires C, 35.47; H, 4.30; N, 6.89%.

K[Fe(Hedta)Cl]·H_2O. This was prepared according to a literature method.[12]

Potentiometric and spectrophotometric studies

All measurements were carried out using solutions of 0.2 mol dm^{-3} ionic strength (KCl) at 25 ± 0.1 °C. Carbonate-free KOH solutions of known concentrations (*ca*. 0.2 mol dm^{-3}) standardised with potassium hydrogen phthalate[13] were used as titrant. The pH-metric titrations were carried out on either a Radiometer pH M84 instrument equipped with a Metrohm 6.0234.100 combined electrode and the titrant added from a Metrohm 715 Dosimat autoburette or on a Molspin pH meter and titration controller with Thermo Russel CMAW711 combined electrode and Hamilton syringe autoburette. In the Ru^{III}-(edta)–hydroxamic acid titrations readings were taken every 3 s to a precision of 0.001 pH units using the Molspin titrator set on 'slow reaction rate'. A minimum number of readings is used to calculate the standard deviation and this is compared to the required precision. This process is repeated between 9 and 900 times until the standard deviation is less than the required precision. This ensures that pH data are collected for a fully equilibrated system.

The electrode system was calibrated by the method of Irving *et al*.[14] (pK_w = 13.734) so that the pH-meter readings could be converted into hydrogen ion concentration.

The pK_a values of the hydroxamic acids and of the aqueous K[Ru(Hedta)Cl]·1.5H_2O system were determined by titrating solutions (~4.0 × 10^{-3} mol dm^{-3}) in HCl (5.0 × 10^{-3} mol dm^{-3}) with a KOH solution of known concentration (0.1961 mol dm^{-3}). The resulting data were analysed using the SUPERQUAD computer program.[15] This method was also used to determine the exact concentration of the ligand and metal stock solutions. Stability constants of the ruthenium(III)–edta–hydroxamate complexes were determined by pH-metric methods using ligand concentrations in the range 1–4 × 10^{-3} mol dm^{-3}, a metal to ligand ratio of 1 : 1 in all cases and data analysed using PSEQUAD[16] and HYPERQUAD.[17] UV-visible spectra for the K[Ru^{III}(Hedta)Cl]·2H_2O + Pha system were obtained on a Helios α Thermo Spectronic spectrophotometer in the region of 200–800 nm, pH 2–10.8, [Ru^{III}] = [Pha] = 0.5 mM, initial volume 100 mL, titrant 0.19849 M KOH. Stability constants were also determined from the spectral data and the spectra of the individual species obtained using PSEQUAD.[16]

The pK_a and stability constant values of K[Fe(Hedta)Cl]·H_2O and of the iron(III)–edta–phenylhydroxamate complex were obtained using the same pH-metric methods.

Crystallography

Crystal data and data collection parameters. X-Ray crystallographic data for hydrated [Ru(H_2edta)(2-OMe-Pha)] were obtained on an Enraf-Nonius CAD-4 diffractometer at 293 K using monochromated Mo-Kα radiation (λ = 0.71073 Å) with the ω–2θ scan method. The structure was solved by direct methods (SHELXS[18]) and refined using full-matrix least squares (SHELXL 97-2[18]), the graphics program used was ORTEP3 for Windows.[19]

Table 1 Selected bond lengths (Å) and angles (°) with estimated standard deviations for [Ru(H_2edta)(2-OMe-Pha)]·4.91H_2O.

Ru(1)–O(2)	1.964(4)	Ru(1)–N(2)	2.060(4)
Ru(1)–O(4)	2.016(4)	Ru(1)–N(3)	2.156(4)
Ru(1)–O(1)	2.019(4)	C(1)–O(1)	1.323(7)
Ru(1)–O(8)	2.044(3)	C(1)–N(1)	1.319(8)
		N(1)–O(2)	1.368(7)
O(2)–Ru(1)–O(4)	94.32(15)	O(4)–Ru(1)–N(3)	91.50(15)
O(2)–Ru(1)–O(1)	81.89(16)	N(2)–Ru(1)–N(3)	84.33(17)
O(4)–Ru(1)–O(1)	93.93(16)	C(1)–O(1)–Ru(1)	110.2(3)
O(4)–Ru(1)–O(8)	173.75(15)	O(1)–C(1)–N(1)	118.9(5)
O(2)–Ru(1)–N(2)	95.95(16)	C(1)–N(1)–O(2)	118.5(5)
O(4)–Ru(1)–N(2)	82.95(16)	N(1)–O(2)–Ru(1)	110.5(3)
O(1)–Ru(1)–N(2)	176.08(13)		

$C_{18}H_{31.82}N_3O_{15.91}Ru$, *i.e.* [Ru($H_2$edta)(2-OMe-Pha)]·4.91$H_2O$, M_r = 645.91, monoclinic, space group *C*2/*c*, a = 42.700(6), b = 8.5319(9), c = 15.292(2) Å, β = 110.264(10)°, V = 5226.2(12) Å^3, Z = 8, D_c = 1.642 Mg m^{-3}, crystal size 0.1 × 0.07 × 0.02 mm, absorption coefficient = 0.68 mm^{-1}, F(000)= 2656.8, T = 93(2) K, θ range for data collection 3.05–23.59°, index ranges $-48 \leqslant h \leqslant 43$, $-9 \leqslant k \leqslant 9$, $-17 \leqslant l \leqslant 17$, reflections collected = 10672, independent reflections = 3739 (R_{int} = 0.1962), completeness to θ = 95.6% (23.59°), absorption correction-semi-empirical from equivalents, max. and min. transmission 1.056 and 0.964, refinement method: full-matrix least-squares on F^2, data/restraints/parameters 3739/0/371, goodness-of-fit on F^2 = 1.110, final R indices [$I > 2\sigma(I)$], $R1$ = 0.1252, $wR2$ = 0.2490, extinction coefficient 0.00093(7), largest diff. peak and hole 1.197 and −0.952 e Å^{-3}. The high R factor is due to a high degree of disorder in the water molecules of hydration. However the bond distances and angles for the complex are quite precise.

Selected bond lengths and angles are listed in Table 1. An ORTEP view of the crystal structure of the complex is shown in Fig. 1.

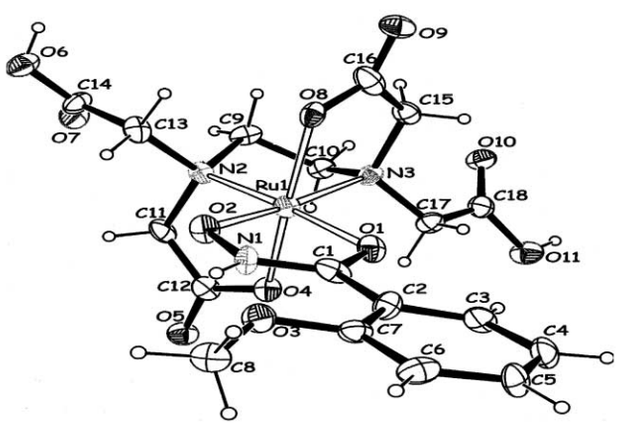


Fig. 1 Crystal structure of [Ru(H_2edta)(2-OMe-Pha)] showing numbering scheme used.

CCDC reference number 210644.

See http://www.rsc.org/suppdata/dt/b3/b310193m/ for crystallographic data in CIF or other electronic format.

Results and discussion

Synthesis and structures

Reaction of hydroxamic acids, R-PhaH, with K[Ru(Hedta)Cl]·1.5H_2O in a 1 : 1 mole ratio in aqueous solution resulted in protonation and decomplexation of a carboxylate arm of the pentadentate Hedta^{3-} ligand and afforded, following concentration of the solutions and cooling, hydroxamate complexes of formula [Ru(H_2edta)(R-Pha)]·$x H_2O$ in good yields. Satisfactory microanalysis for all complexes were obtained.

The crystal and molecular structure of hydrated [Ru(H_2edta)-(2-OMe-Pha)], the only complex which gave crystals suitable for X-ray diffraction studies, was determined. Although the R indices are relatively high due to disorder in the solvent molecules all bond lengths and angles in the complex are quite precise and the results clearly establish the structure of this, the first ruthenium(III)–hydroxamate to be structurally characterised. In this complex H_2edta is present as a tetradendate, dianionic ligand coordinated in a 2N, *trans*-2O (dicarboxylato) manner with two uncoordinated carboxylic acid groups. The hydroxamate ligand shows normal O,O-bidentate coordination. The Ru–O (carboxylate) bond lengths of 2.016(4) and 2.044(3) Å are similar to those for the *trans* carboxylato groups in NH_4[Ru(Hedta)Cl], 2.020(4) and 2.008(4) Å,[11] while the Ru–N bond *trans* to the negatively charged hydroxamate oxygen, 2.156(4) Å, is slightly longer than the Ru–N bond *trans* to the hydroxamate carbonyl oxygen, 2.060(4) Å. Different Ru–N bond distances were previously reported for NH_4[Ru(Hedta)-Cl],[11] Ru–N 2.049(4) and 2.116(4), and attributed to the fact that one nitrogen atom is part of three chelate rings while the other is only part of two. In the present complex however this is not the case as the H_2edta ligand is symmetrical and the difference in bond lengths may be due to the *trans*-influences of the anionic hydroxamate oxygen being greater than that of the carbonyl oxygen. A *trans* influence in ruthenium(III) complexes has previously been invoked to explain similar differences in Ru(III)–N bond lengths in Ru(edta)(NO) and Ru(Hedta)-(H_2O).[20] The Ru–O (hydroxamate) bond is slightly shorter than the Ru–O (carboxylate) bonds. The C=O and C–N bond lengths in the hydroxamate ligand are similar to those reported for iron(III),[21] copper(II)[22] and nickel(II)[23] hydroxamate complexes and are intermediate between expected single and double bond lengths indicative of delocalisation of the nitrogen lone pair into the π-electron system.

The IR spectra of [Ru(H_2edta)(2-OMe-Pha)]·2H_2O and the other complexes synthesized showed distinct bands at ~3350 and 2950 cm^{-1} due to ν(NH), ~1730 cm^{-1} due to $\nu(C{=}O)_{COOH}$, ~1640 cm^{-1} due to $\nu(C{=}O)_{COO^-}$ and ~1605 cm^{-1} due to $\nu(C{=}O)_{CONHO^-}$ indicating that all have similar structures.

Formation constants and species distribution curves

Species distribution and formation constants for the binary Ru(III)–edta and the ternary Ru(III)–edta–hydroxamate complexes were investigated by pH-metric studies and by UV-VIS spectrophotometric methods at 25 ± 0.1 °C, and ionic strength 0.2 mol dm^{-3} (KCl). pK_a values for the hydroxamic acids were also obtained under the same conditions. The pK_a values of the hydroxamic acids, Table 2, compare favourably with previously reported values.[24]

The binary [Ru(Hedta)Cl]$^-$ system. In aqueous solution the complex [Ru(Hedta)Cl]$^-$ undergoes rapid hydrolysis to give [Ru(Hedta)(OH_2)]. The species distribution diagrams for this system are presented in Fig. 2 and the pH titration in Fig. 3(a). The pK_a values of this complex were found to be 2.41(1) for the free carboxylic acid group of the Hedta ligand and 7.34(1) for the aqua ligand. These agree favourably with literature reported values.[25] At higher pH, an additional hydrolytic process, not reported previously, was observed. This has a pK_a value of 10.22(1) and is most likely due to replacement of one of the bound carboxylate groups of edta by a second hydroxide leading to [Ru(edta)$(OH)_2]^{3-}$.

The ternary [Ru(Hedta)Cl]$^-$/hydroxamate systems. The titration curve for the ternary Pha–[Ru(Hedta)Cl]$^-$ system, as a representative example, is shown in Fig. 3(a) and compared with those for free Pha and the binary [Ru(Hedta)Cl]$^-$ system. These titration curves are typical of all the unsubstituted hydroxamic acids studied. In the ternary system there are three

Table 2 Overall stability constants ($\log\beta$ values[a]) and selected stepwise stability constants ($\log K$[b]) of ruthenium(III)–hydroxamate complexes, I = 0.20 mol dm^{-3} and T= 25.0 °C (standard deviations given in parentheses).

$\log\beta$	$M_pA_qH_r$	Acha	*N*-MeAcha	Pha	2-OMe-Pha	4-OMe-Pha	2-Me-Pha	4-Me-Pha	4-OH-Pha
HL	0 1 1	9.27(1)	8.67(3)	8.66(1)	8.88(1)	8.93(1)	8.73(1)	8.85(2)	9.78(1)
H_2L	0 1 2								18.11(1)
M(HL)[c]	1 1 1	–	–	–	–	–	–	–	16.49(1)[c]
ML[d]	1 1 0	7.14(1)	6.82(4)	7.28(1)	7.47(1)	7.23(1)	7.25(1)	7.32(1)	–
				7.07(1)[e]					
$M(HL)H_{-1}$	1 1 0	–	–	–	–	–	–	–	8.99(1)
MLH_{-1}	1 1 –1	–0.44(1)	–	0.60(1)	–0.27(2)	0.11(1)	0.28(1)	0.17(1)	–0.44(1)
				0.08(3)[e]					
$MLH_{-1}(OH)$	1 1 –2	–11.07(1)	–	–9.71(1)	–10.78(2)	–11.08(1)	–11.26(2)	–11.27(3)	–12.08(2)
				–9.2(2)[e]					
$\log K$									
$ML \rightleftarrows MLH_{-1}$		–7.58	–	–6.68	–7.74	–7.12	–6.97	–7.15	–7.50
$MLH_{-1} \rightleftarrows MLH_{-1}(OH) + H^+$		–10.63	–	–10.31	–10.51	–11.19	–11.54	–11.46	–11.64

[a] $\log\beta$ values refer to the equilibrium $pM + qL + rH \rightleftarrows M_pL_qH_r$. [b] $\log K$ values refer to the equilibrium $M_pL_qH_r \rightleftarrows M_pL_qH_{(r-1)}$. [c] M(HL) = 4-OH-Pha (*i.e.* H refers to phenolic proton). [d] M = Ru^{III}(edta). [e] Determined from spectrophotometric data by PSEQUAD.[16] Because of potential errors in the spectrophotometric data, *e.g.* the solutions used were unbuffered and pH values may have fluctuated while recording spectra, the standard deviations quoted for these constants are underestimates.

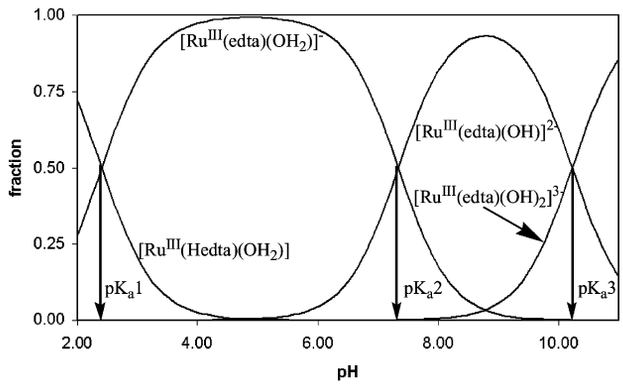


Fig. 2 Concentration distribution curves for the Ru^{III}–edta/H^+ (binary) system, pH 2–11, [Ru^{III}] = 0.002 M.

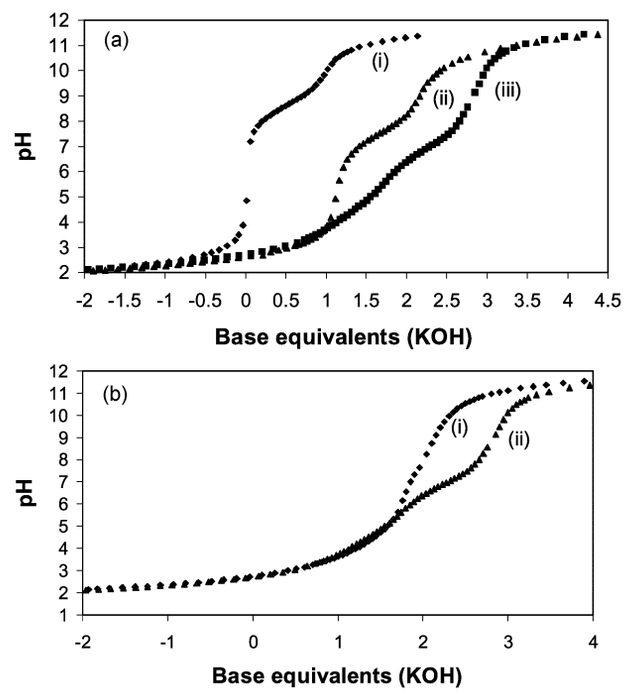


Fig. 3 (a) Titration curve (pH *vs.* base equivalents) for (i) Pha, (ii) K[Ru(Hedta)Cl]·1.5H_2O and (iii) Pha+K[Ru(Hedta)Cl]·1.5H_2O. (b) Titration curve for (i) *N*-MeAcha + K[Ru(Hedta)Cl]·1.5H_2O and (ii) Pha + K[Ru(Hedta)Cl]·1.5H_2O.

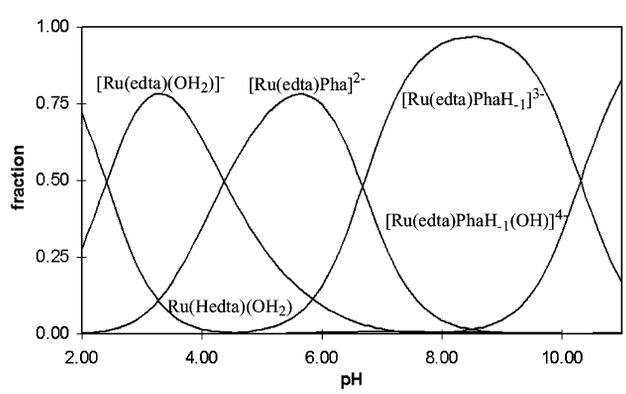
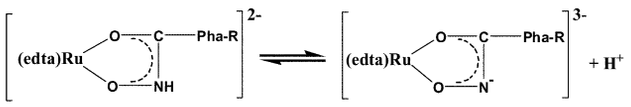


Fig. 4 Concentration distribution curves for the K[Ru(Hedta)Cl]·1.5H_2O + Pha system, pH 2–11, L/M = 1, [Ru^{III}] = 0.002 M.

dissociable protons below pH 10 the first two corresponding to deprotonation of the Hedta ligand and the hydroxamic acid leading to $[Ru(edta)(Pha)]^{2-}$, the major species in solution in the pH range 4.5–7, Fig. 4. The third ionisation, in weakly alkaline solution, is due to deprotonation of the NH group in the coordinated hydroxamate giving $[Ru(edta)(PhaH_{-1})]^{3-}$



Scheme 1

which contains the dianionic hydroximate ligand, Scheme 1. This is confirmed by the fact that a pH-titration of the *N*-methylacetohydroxamic acid–[Ru(Hedta)Cl]$^-$ system which lacks the NH hydroxamate proton showed no such ionisation, Fig. 3(b). Further proof of this is that the ionisation, as expected, is accompanied by marked changes in the hydroxamate ligand to metal charge transfer band in the visible spectrum. The formation of the ternary complex [Ru(edta)(Pha)]$^{2-}$ between pH 3 and 6 is characterised by a colour change from yellow to red and the appearance of a hydroxamate ligand-to-metal charge transfer band having λ_{max} ~485 nm, Fig. 5. With increasing pH (6.5–9) the solution changes from red to purple and the absorption band shifts to longer wavelength, λ_{max} ~546 nm. This shift which was not observed for [Ru(edta)(*N*-MeAcha)]$^{2-}$, Fig. 6, is indicative of more facile charge transfer and consistent with the formation of [Ru(edta)(PhaH$_{-1}$)]$^{3-}$. At pH >10 a further mole of base is consumed and this is attributed to reversible formation of [Ru(edta)(PhaH$_{-1}$)(OH)]$^{4-}$. This process causes very little change in the visible spectrum indicating that the hydroxy ligand displaces a coordinated carboxylate of edta rather than the hydroxamate ligand.

The stability constants of the aromatic hydroxamate complexes [Ru(edta)(R-Pha)]$^{2-}$, ML, obtained pH-metrically,

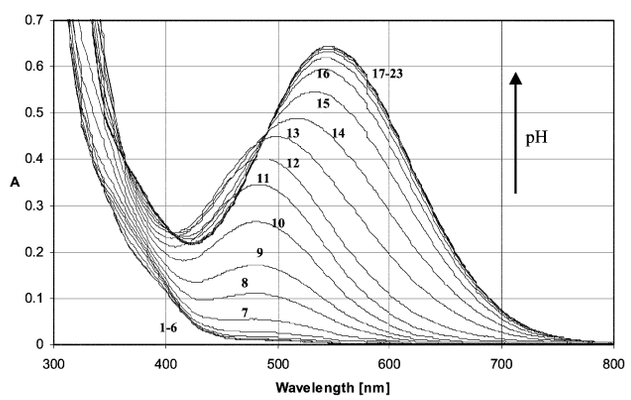


Fig. 5 UV-Vis spectra of K[Ru^{III}(Hedta)Cl]·1.5H$_2$O + Pha, pH 2–10.8, [Ru^{III}] = [Pha] = 0.5 mM, initial volume 100mL, titrated with 0.19849 M KOH; spectra 1–6: pH 2.00–4.00 (~0.40 pH intervals), spectra 7–16: pH 4.86–8.02 (~0.40 pH intervals), spectra 17–23: pH 8.40–10.79 (~0.40 pH intervals). Spectra were recorded over a 9 h period. Analysis of the data using PSEQUAD,[16] gave stability constants (Table 2) and spectra of the individual species as follows: [Ru(edta)(Pha)]$^{2-}$, λ_{max} = 480 nm, ε = 1260 mol^{-1} dm^3 cm^{-1}; [Ru(edta)(PhaH$_{-1}$)]$^{3-}$, λ_{max} = 544 nm, ε = 1523 mol^{-1} dm^3 cm^{-1} and [Ru(edta)(PhaH$_{-1}$)(OH)]$^{4-}$, λ_{max} = 545, ε = 1526 mol^{-1} dm^3 cm^{-1}.

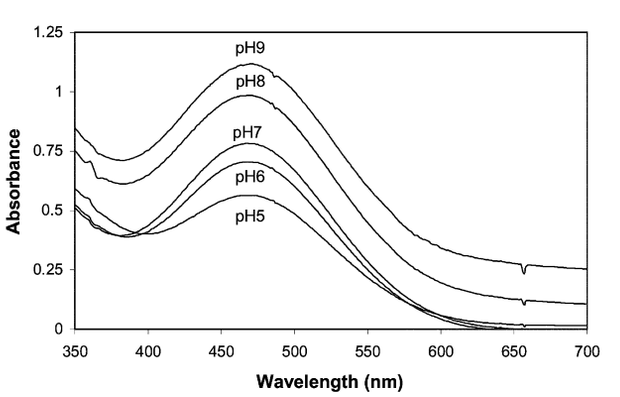


Fig. 6 UV-Vis spectra of *N*-methylacetohydroxamic acid + K[Ru(Hedta)Cl]·1.5H$_2$O, pH 5–9, [Ru^{III}] = 0.002 M.

Table 2, lie between 7.28(1) and 7.47(1) and in general correlate with ligand basicity. These complexes however are more stable than the acetohydroxamate complex despite the significantly higher basicity of this ligand. The pK_a values for ionisation of the hydroxamate ligands in the complexes [Ru(edta)(R-Pha)]$^{2-}$, Scheme 1, which lie in the range 6.68–7.74, also correlate with ligand basicity with the exception of the 2-OMe-Pha complex for which the pK_a value, 7.74, is much higher than the others. This may be due to hydrogen bonding between the hydroxamate NH group and the ether O, which stabilises the hydroxamate relative to the hydroximate complex. The pK_a value for ionisation of the acetohydroxamate complex is significantly higher than the phenylhydroxamate complex as expected from the relative ligand basicities. The pK_a values for the formation of the hydroxo complexes [Ru(edta)(R-PhaH$_{-1}$)(OH)]$^{4-}$ lie in the range 10.31–11.64. Although the primary aim of carrying out the pH-dependent spectrophotometric study (Fig. 5) was to establish that base consumption in near neutral solution was due to ionisation of the hydroxamate ligand (see above and Scheme 1), stability constants were also obtained by analysis of these data by PSEQUAD[16] for the phenylhydroxamate complex. The conditions used for the spectrophotometric study were as close as possible to those for the pH-metric study but the logβ values obtained differed by 0.21–0.52 units, Table 2. However because of potential errors in the spectrophotometric data, *e.g.* the solutions used were unbuffered and pH values may have fluctuated while recording spectra, the stability constants obtained pH-metrically are much more reliable. The spectra of the individual species were also obtained, Fig. 5, from which it can be seen that the spectra of [Ru(edta)(PhaH$_{-1}$)]$^{3-}$ and [Ru(edta)(PhaH$_{-1}$)(OH)]$^{4-}$, in which an OH$^-$ ligand has displaced a coordinated carboxylate of edta, are almost identical.

The concentration distribution curves for the ternary system involving Pha as a representative example are shown in Fig. 4. The yellow-coloured Ru^{III}–edta complex reacts with hydroxamate from pH ~3 to give the red [Ru(edta)(Pha)]$^{2-}$ which is the major species at pH 4.5–7 and reaches maximum concentration at pH 6 where deprotonation of the hydroxamate NH group commences. This gives the purple-coloured hydroximato complex [Ru(edta)(PhaH$_{-1}$)]$^{3-}$, the major species in solution at pH 7–10. At pH > 10 formation of the hydroxo complex [Ru(edta)(PhaH$_{-1}$)(OH)]$^{4-}$ is observed.

Reports on deprotonation of hydroxamate to hydroximato ligands in mononuclear complexes are indeed very limited (several examples have been reported of oligonuclear metallacrown complexes containing bridging hydroximato ligands[26]) having previously been observed in the case of the acetohydroxamate and phenylhydroxamate (L) complexes [CuL(LH$_{-1}$)]$^-$ and [Cu(LH$_{-1}$)$_2$]$^{2-}$ identified at high pH by EPR spectroscopy,[27] [VO(LH$_{-1}$)$_2$]$^{2-}$ and [V(LH$_{-1}$)$_3$]$^{2-}$ also identified by EPR spectroscopy,[28] in molybdenum(VI)–acetohydroxamate systems where the species [MoO$_2$(LH$_{-1}$)(OH)$_2$]$^{2-}$, [MoO$_3$(LH$_{-1}$)(H$_2$O)]$^{2-}$ and [MoO$_3$(LH$_{-1}$)(OH)$_2$]$^{2-}$ were identified by ^{17}O and ^{1}H NMR spectroscopy[29] and in manganese(IV)–phenylhydroxamate and manganese(III)–anthranilic hydroxamate systems where salts of the complexes [Mn(LH$_{-1}$)$_3$]$^{2-}$ and [Mn(LH$_{-1}$)$_2$]$^-$, respectively, were isolated.[30] The scarcity of information on such systems is at least partly due to the general insolubility of metal–hydroxamate complexes. This problem was not encountered in the present case and relevant equilibria for a series of hydroxamate complexes are reported.

The pK_a value of 7.58 for the acetohydroxamate complex [Ru(edta)(Acha)]$^{2-}$ is comparable to the values (albeit measured under different conditions) of 6.74 reported for [MoO$_2$(Acha)(OH)$_2$)]$^-$ and 7.73 for [MoO$_3$(Acha)(H$_2$O)].

Nitrosyl abstraction from hydroxamic acids

As previously reported by us, ruthenium(III) complexes such as [Ru(Hedta)Cl]$^-$ abstract NO from hydroxamic acids on heating,

to give the ruthenium(II)–nitrosyl complex $[Ru^{II}(edta)(NO)Cl]^-$ and the corresponding carboxylic acids.[7] The proposed mechanism for this reaction involves initial formation of a $[Ru^{III}(edta)(hydroxamate)]^{2-}$ complex followed by hydroxide attack on the carbonyl carbon of the hydroxamate complex giving a tetrahedral intermediate, cleavage of the C–N bond of which causes release of hydroxylamine, a known source of NO.[31] In the case of the more acidic ligands such as 2-nitro-, 4-nitro- and 2-chloro-phenylhydroxamic acid, irreversible formation of nitrosyls was observed in the pH range 3–6 during the pH-metric measurements at 25 °C. This was accompanied by a colour change from orange/yellow to brown and by the appearance of a shoulder at around 390 nm in the visible spectrum. Because of competing nitrosyl formation stability constants could not be determined for ternary systems involving these hydroxamic acids.

Comparison of Ru(III)–hydroxamate and Fe(III)–hydroxamate systems

In order to compare the binding affinities of ruthenium(III) and iron(III) towards hydroxamate ligands it was decided to carry out speciation studies on the Fe^{III}(edta)–Pha system. The binary Fe^{III}–edta system has been thoroughly investigated.[12,32] The hexacoordinated species $[Fe(Hedta)(H_2O)]$ which exists at low pH is sequentially converted to the heptacoordinated species $[Fe(edta)(H_2O)]^-$, $[Fe(edta)(OH)]^{2-}$ and $[Fe(edta)(OH)_2]^{3-}$ on raising pH, the first two species containing hexadentate and the last containing pentadentate $edta^{4-}$. Species distribution curves for the Fe^{III}–edta–Pha ternary system are presented in Fig. 7. In contrast to $[Ru(edta)(Pha)]^{2-}$ which starts to form at pH less than 3 and is a major species at pH 4–7, $[Fe(edta)(Pha)]^{2-}$ does not start to form until pH greater than 5 and does not become a major species until pH 7.5. The overall stability constant for $[Ru(edta)(Pha)]^{2-}$, 7.28(1), is much greater than that of $[Fe(edta)(Pha)]^{2-}$, 4.41(2), Table 3, indicating that Pha has a much higher affinity for $[Ru(edta)(H_2O)]^-$ than it has for $[Fe(edta)(H_2O)]^-$. However it must be borne in mind that the reactions involved in the formation of the ternary complexes are significantly different as are the structures of the products. The formation of $[Ru(edta)(Pha)]^{2-}$ involves reaction of Pha with the overall neutral, hexacoordinated environment $Ru^{III}(N_2O^-_3)O$ in $[Ru(edta)(H_2O)]^-$ whereas formation of $[Fe(edta)(Pha)]^{2-}$, involves reaction with the anionic heptacoordinated environment $Fe^{III}(N_2O^-_4)O$ in $[Fe(edta)(H_2O)]^-$. The charge and coordination number differences of the immediate metal coordination environment of the reactants would contribute significantly to a lower stability constant for the iron complex. It is noteworthy that the third stepwise stability constant of $Fe(Pha)_3$, 7.60(8),[24b] which involves reaction of Pha with hexacoordinated $[Fe(Pha)_2(H_2O)_2]^+$, is comparable to that of $[Ru(edta)(Pha)]^{2-}$, particularly if allowance is made for the effect of charge difference in the immediate coordination environments of the reacting species, *i.e.* the positively charged $Fe^{III}(OO^-)_2O_2$ relative to the neutral $Ru^{III}(N_2O^-_3)O$.

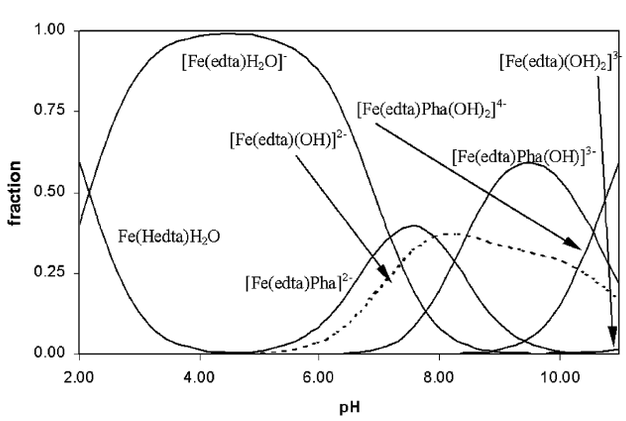


Fig. 7 Concentration distribution curves for the $K[Fe(Hedta)Cl]\cdot H_2O$ + Pha system, pH 2–11, L/M=1, $[Fe^{III}] = 0.002$ M.

Table 3 Protonation and hydrolysis constants of $K[M^{III}(Hedta)Cl]\cdot xH_2O$ and overall stability constants for complexes formed in M^{III}–edta–Pha systems (where $M^{III} = Ru^{III}$, Fe^{III}), $I = 0.20$ mol dm^{-3} and $T = 25.0$ °C (standard deviations given in parentheses)

Species	$M_pA_qH_r$	Ru^{III}	Fe^{III}
$M(Hedta)(OH_2)$	1 0 1	2.41(1)	2.17(1)
M(edta)(OH)	1 0 −1	−7.34(1)	−7.36(1)
$M(edta)(OH)_2$	1 0 −2	−17.56(1)	−19.36(3)
M(edta)(Pha)	1 1 0	7.28(1)	4.41(2)
$M(edta)(PhaH_{-1})$	1 1 −1	0.60(1)	–
M(edta)(Pha)(OH)	1 1 −1	–	−3.84(1)
$M(edta)(PhaH_{-1})(OH)$	1 1 −2	−9.71(1)	–
$M(edta)(Pha)(OH)_2$	1 1 −2	–	−14.40(1)

In contrast to the octahedral $[Ru(edta)(Pha)]^{2-}$ the complex $[Fe(edta)(Pha)]^{2-}$ is probably heptacoordinated since the band at ~460 nm in the solution spectrum is of much lower intensity (ε ~130 dm^3 mol^{-1} cm^{-1}) than expected for an octahedral complex containing bidentate hydroxamate. This is consistent with the higher tendency of edta to maintain pentadenticity in iron(III) relative to ruthenium(III) complexes, as evidenced by the much greater number of edta complexes of Ru(III) having denticity lower than five compared to iron(III). The complex $[Fe(edta)(Pha)]^{2-}$ undergoes two hydrolytic processes in alkaline solution with pK_a values of 8.25(1) and 10.56(1).

Conclusions

In this paper we report the structure of the first ruthenium(III)–hydroxamate complex, hydrated $[Ru(H_2edta)(2\text{-}OMe\text{-}Pha)]$, and the synthesis and characterisation of several others. We describe also speciation curves and stability constants for binary $[Ru(Hedta)Cl]^-$ and ternary $[Ru(edta)(hydroxamate)]^{2-}$ systems and the further deprotonation of hydroxamate ligands in weakly basic solution to give a series of hydroximato complexes hitherto reported in only a few instances. We also compare the relative affinities of Ru(III) and Fe(III) for hydroxamate ligands.

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