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Ruthenium Tris Chelates with O,S-Siderophores: Synthesis, Oxidation State, and Electronic Structure

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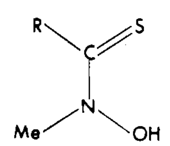
N-Methylthiohydroxamic acids (RC(S)N(OH)Me), abbreviated HmeR (R = Ph, *p*-C_6H_4OMe, CH_2Ph), react with $RuCl_3{\cdot}3H_2O$ in aqueous ethanol affording the green tris chelates $Ru^{III}(meR)_3$. Cerium(IV) oxidation of these complexes in perchlorate media furnishes reddish pink $Ru^{IV}(meR)_3ClO_4{\cdot}H_2O$. The ruthenium(IV)–ruthenium(III) formal potential ($E°_{298}$) determined cyclic voltammetrically is ~0.4 V vs. SCE. The wine red ruthenium(II) species $Ru(meR)_3^-$ are also accessible voltammetrically but are too unstable to be isolated. $E°_{298}$ of the ruthenium(III)–ruthenium(II) couple is ~−1.0 V. Both redox couples are nearly reversible, suggesting the same gross stereochemistry for the three oxidation states. On the basis of comparative X-ray powder and IR data it is concluded that $Ru(meR)_3$ has facial stereochemistry. The $Ru(meR)_3$ complexes are low spin ($S = {}^1/_2$; $t_2{}^5$) and have rhombic EPR spectra. The axial distortion parameter Δ is found to be large and positive (~6000 cm^{-1}). The ground state is nearly pure A in character. The rhombic splitting is ~1500 cm^{-1}. In near-IR spectra $Ru(meR)_3$ has a weak ($\epsilon \sim 100$) band at ~1500 nm with signs of a second band at lower energies. These are assigned to transitions within the Kramers doublets. The ruthenium(IV) cation $Ru(meR)_3^+$ is paramagnetic ($S = 1$; $t_2{}^4$) but is EPR silent, probably due to fast relaxation. The thiohydroxamic acid PhC(S)N(OH)H, abbreviated H_2ph, affords low-spin red-violet $Na[Ph_4As]_2[Ru^{III}(ph)_3]{\cdot}H_2O$ and blue $Na[Ph_4As][Ru^{IV}(ph)_3]{\cdot}H_2O$. Here the ruthenium(IV)–ruthenium(III) formal potential is unusually low, −0.16 V, and the ruthenium(III)–ruthenium(II) $E°_{298}$ is −1.17 V. The EPR spectrum of $Ru(ph)_3^{3-}$ is rhombic but the three *g* values are closely spaced near 2 compatible with large net distortion. Two low-intensity optical bands at 1430 and 1180 nm corresponding to transitions within the Kramers doublets can be recovered by Gaussian analysis. The $Ru^{IV}(ph)_3^{2-}$ ion undergoes a nearly reversible one-electron oxidation ($E°_{298}$ = 0.62 V) to deep blue, unstable, and EPR-active $Ru(ph)_3^-$ (a slightly asymmetric signal at $g \sim 2$). Two descriptions, viz. the ruthenium(IV)-stabilized ligand radical complex $Ru^{IV}(ph)_2(ph{\cdot})^-$ and the ruthenium(V) complex $Ru^V(ph)_3^-$, are examined. The EPR spectrum is not incompatible with either description, but the $Ru^V(ph)_3^-$ description has more favorable features. The thiohydroximate ligand appears to be able to span all oxidation states of ruthenium from +2 to +5.

Introduction

This work stems from our interest in the ruthenium chemistry of the siderophore class of ligands. A model family in this class is represented by hydroxamic acids (–C(O)N(OH)– functionality), which play a crucial role in bacterial iron transport.[1] Hence the notable recent development in the chemistry of transition-metal hydroxamates and hydroximates, particularly due to the efforts of Raymond and co-workers.[2] We have described complexes of this family for ruthenium,[3,4] iron,[5] and molybdenum.[6] The discovery[7] that antibiotic copper(II) and iron(III) chelates of a thiohydroxamic acid (–C(S)N(OH)– functionality) are biologically producible has provided incentive for substantial activity[8–20] in the transition-metal chemistry of this new class of siderophores. In this paper we describe for the first time the thiohydroxamates and thiohydroximates of ruthenium with special reference to synthesis, stereochemistry, electronic structure, redox behavior, and metal oxidation states.

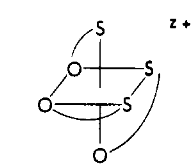
Results and Discussion

A. Tris(thiohydroxamato) Complexes. In this and the subsequent three sections we shall be concerned with thiohydroxamates of ruthenium derived from three ligands of type **1**. Subsequently thiohydroximates will be considered in a separate



R = Ph (HmePh)
R = $C_6H_4OMe(p)$ (HmeAn)
R = CH_2Ph (HmeBz)

1



z = 0,1

2

section. The ligands of type **1** are generally abbreviated as HmeR, specific abbreviations for the three ligands used in the present work are as shown in **1**. The dissociable[21] OH proton in HmeR is invariably ionized on complex formation.

The green tris chelates of type $Ru^{III}(meR)_3$ precipitate on reacting $RuCl_3{\cdot}3H_2O$ with HmeR in acidic aqueous ethanol at ~280 K. The chemical oxidation of $Ru(meR)_3$ was achieved by using cerium(IV) ion in acidic solution as the oxidant. The reddish pink oxidized complex $Ru^{IV}(meR)_3^+$ was isolated as the perchlorate monohydrate.

The various complexes synthesized and their characterization data are given in Table I. In acetonitrile solution $Ru(meR)_3$ is a nonelectrolyte, while $Ru(meR)_3ClO_4{\cdot}H_2O$ acts as an 1:1 electrolyte. Magnetic moment data are compatible with pseudooctahedral (**2**) low-spin d^5 ($S = {}^1/_2$) and d^4 ($S = 1$) configurations for $Ru(meR)_3$ (in contrast $Fe(meR)_3$ is high spin[16,18]) and $Ru(meR)_3^+$, respectively. Both types of complexes display a number of absorption bands in the region 300–2500 nm (Table I) some of which will be further examined in a latter section.

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Table I. Selected Physical Data of the Complexes

compd	molar conductivity[a] Λ, Ω^{-1} cm^2 M^{-1}	μ_{eff}, μ_B	electronic spectral data[a] λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$Ru(mePh)_3$	*b*	1.85	1500 (110), 640 (1340), 470[c] (1900), 350 (7100)
$Ru(meAn)_3$	*b*	1.77	1500 (80), 635 (1240), 470[c] (2000), 355[c] (8500)
$Ru(meBz)_3$	*b*	1.80	1500 (70), 630 (1200), 470[c] (1500), 330 (7200)
$[Ru(mePh)_3]ClO_4 \cdot H_2O$	165	2.82	1200[c] (480), 840 (2100), 520 (3700)
$[Ru(meAn)_3]ClO_4 \cdot H_2O$	185	2.84	1200[c] (480), 840 (2000), 530 (3850), 470[c] (3650)
$[Ru(meBz)_3]ClO_4 \cdot H_2O$	170	2.91	1200[c] (450), 820 (2200), 515 (4200)
$Na[Ph_4As]_2[Ru(ph)_3] \cdot H_2O$	345	1.90	1325[c] (480), 1100[c] (880), 830 (2290), 510 (5800), 340[c] (12800)
$Na[Ph_4As][Ru(ph)_3] \cdot H_2O$	260	2.82	1075 (2300), 650[c] (4000), 555 (7200)

[a] Solvent is CH_3CN. [b] Nonelectrolyte. [c] Shoulder.

Table II. Electrochemical Data[a] at 298 K

compd	$E°_{298}$,[b] V (n[c])
$Ru(mePh)_3$	0.37 (0.98),[d] −1.00 (0.97)[e]
$Ru(meAn)_3$	0.29 (0.98),[d] −1.08 (0.99)[e]
$Ru(meBz)_3$	0.34 (1.01),[d] −1.04 (0.98)[e]
$Na[Ph_4As]_2[Ru(ph)_3] \cdot H_2O$	0.62,[f] −0.16 (1.01),[g] −1.17 (1.03)[h]

[a] The working electrode is platinum, the solvent is CH_3CN, the supporting electrolyte is TEAP (0.1 M), and the standard is SCE. [b] Cyclic voltammetric data at scan rate of 50 mV s^{-1} and solute concentration $\sim 10^{-3}$ M: $E°_{298}$ is calculated as the average of anodic and cathodic peak potentials. [c] $n = Q/Q'$ where Q' is the calculated coulomb count for 1e transfer and Q is the coulomb count found after exhaustive electrolysis of 0.01 mmol of solute. [d] Oxidation was performed at 0.6 V. [e] Reduction was performed at −1.2 V. [f] A reliable n value could not be determined due to continuous accumulation of coulombs at 0.7 V and above. [g] Oxidation was performed at 0.2 V. [h] Reduction was performed at −1.3 V.

B. Redox Potentials. The formal potential ($E°_{298}$) of couple 1 determined cyclic voltammetrically in acetonitrile solution (0.1

$$Ru^{IV}(meR)_3^+ + e^- \rightleftharpoons Ru^{III}(meR)_3 \quad (1)$$

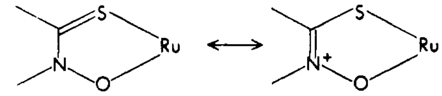
$$Ru^{III}(meR)_3 + e^- \rightleftharpoons Ru^{II}(meR)_3^- \quad (2)$$

M TEAP; platinum electrode) is $\sim$0.4 V vs. saturated calomel electrode (SCE). A second response seen near −1.0 V is assigned to couple 2 (Figure 1; Table II). Both processes are nearly reversible with peak-to-peak separations of 60–80 mV at scan rates of 50 mV s^{-1} to 1 V s^{-1}. This strongly suggests that all the three species have the same gross stereochemistry.

The one-electron character of couples 1 and 2 were confirmed coulometrically (Table II). The wine red solutions of $Ru(meR)_3^-$ are thermally unstable apart from being sensitive to air. Thus the coulometric cycling between $Ru(meR)_3^+$ and $Ru(meR)_3$ can be done many times without any degradation. This is not so for the $Ru(meR)_3$, $Ru(meR)_3^-$ pair due to the instability of the latter. No attempts were made to isolate $Ru(meR)_3^-$ in the pure state as salts.

We note in passing that the iron analogues of both couples 1 and 2 are observable as nearly reversible responses in cyclic voltammetry. The formal potentials are as follows: $Fe(mePh)_3$ −0.73, 0.66 V; $Fe(meAn)_3$ −0.72, 0.60 V. Only couple 2 has been reported in the literature.[17]

C. Stereochemistry. Since ligand **1** is unsymmetrical, the tris chelates can in principle occur in facial (cis) and meridional (trans) forms. Our crude $Ru(meR)_3$ preparations did not give any indication of being isomeric mixtures during chromatographic purification, and in all cases only one isomer could be isolated. Except for small shifts in frequencies, the infrared spectrum (400–4000 cm^{-1})[22,23] of $Ru(mePh)_3$ is *superposable* on those of the structurally characterized[14] *cis*-$Fe(mePh)_3$ and *cis*-$Co(mePh)_3$. Further the ruthenium complex can be freely doped (vide infra) into *cis*-$Co(mePh)_3$ by cocrystallization from solution. Finally $Ru(mePh)_3$ and *cis*-$Co(mePh)_3$ display isomorphous X-ray powder patterns (Table III). These are strong indications that $Ru(mePh)_3$—and by inference the other $Ru(meR)_3$ species—has the chelate ring **3** (with **3b** as the major contributor[14,15]) arranged



3a 3b

in facial stereochemistry,[24,25] **2**. We assume that this also applies

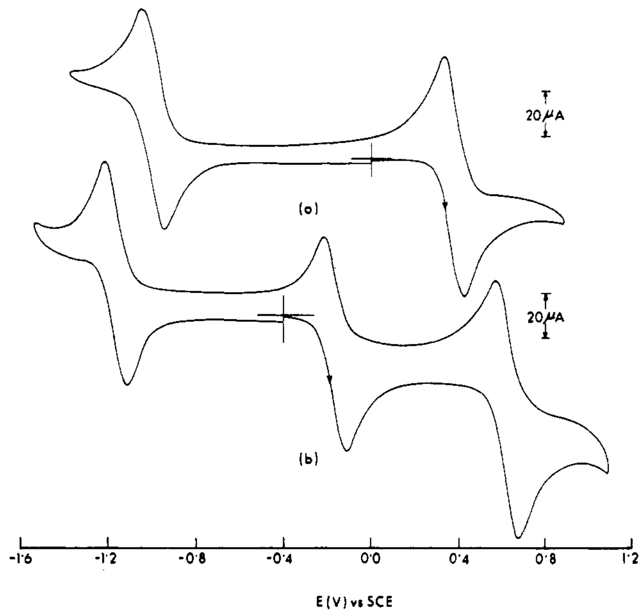


Figure 1. Cyclic voltammograms in CH_3CN (0.1 M TEAP) at a platinum working electrode at a scan rate of 50 mV s^{-1} (298 K) of (a) $[Ru(mePh)_3]$ (1.41 × 10^{-3} M) and (b) $Na[Ph_4As]_2[Ru(ph)_3] \cdot H_2O$ (0.98 × 10^{-3} M).

Table III. X-ray Powder Data[a,b] of $Ru(mePh)_3$: *d*, Å

10.39 (10.31), 9.24 (9.24), 7.60 (7.62), 6.33 (6.33), 5.66 (5.64), 5.17 (5.17), 4.39 (4.36), 4.13 (4.03), 3.71 (3.77), 3.55 (3.56), 3.40 (3.44), 3.29 (3.23), 3.00 (3.05), 2.84 (2.90), 2.73 (2.75), 2.62 (2.65), 2.48 (2.51), 2.35 (2.32), 2.20 (2.21), 2.12 (2.10), 2.05 (2.04), 1.90 (1.91)

[a] Cu Kα, λ = 1.5418 Å, radiation was used. [b] Data in parentheses are those of $Co(mePh)_3$.

(22) The infrared spectra of metal thiohydroxamates are usually complex, and definitive assignments are difficult to make.[10,11,23]

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(24) The facial $M(mePh)_3$ (M = Cr, Fe, Co) complexes all display distortions toward the trigonal-prismatic geometry.[14,15] The molecular site symmetry is however only approximately C_3, showing that small rhombic distortions also coexist. The trigonal distortion decreases in the order Fe < Cr < Co in accord with field predictions.[25] By the same token the low-spin d^5 configuration should be more susceptible to this distortion than the low-spin d^6 (as in $Co(meR)_3$) case. But in going from the 3d to 4d series (for a given d^n configuration) trigonal distortion is expected to be dampened by the increase in the value of Dq. Thus the trigonal distortion in $Ru(meR)_3$ (low-spin $4d^5$) is not expected to be large.

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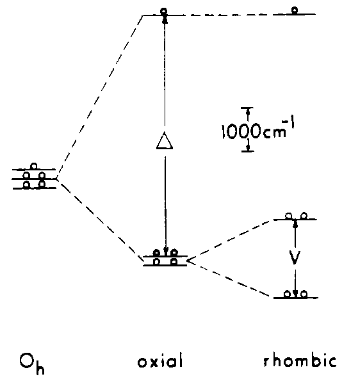

Figure 2. Axial and rhombic splitting of the t_2 level drawn to scale for the case of [Ru(mePh)$_3$] (see text).

Table IV. Observed g Values[a] of Ruthenium(III) Complexes

compd	g_1	g_2	g_3
Ru(mePh)$_3$	2.178	2.109	1.907
	2.156[b]	2.102[b]	1.907[b]
Ru(meAn)$_3$	2.175	2.112	1.911
Ru(meBz)$_3$	2.177	2.110	1.913
Na[Ph$_4$As]$_2$[Ru(ph)$_3$]·H$_2$O[c]	2.093	2.051	2.003

[a] Unless otherwise mentioned measurements were in 1:1 chloroform–toluene glass at 77 K. [b] In Co(mePh)$_3$ matrix (1%, 77 K). [c] In 1:1 acetonitrile–toluene glass at 77 K.

to Ru(meR)$_3^+$. Its electrochemical formation from Ru(meR)$_3$ is nearly Nernstian (vide supra) and there is a 1:1 correspondence in the IR bands of Ru(mePh)$_3$ and Ru(mePh)$_3$ClO$_4$·H$_2$O except that the latter shows extra bands due to lattice water (3400 cm^{-1}) and ionic perchlorate (1090 and 625 cm^{-1}). The cation Ru(meR)$_3^+$ is of special interest since tris chelates of ruthenium(IV) are rare.[26] Seven-coordinated dithiocarbamates, Ru(dtc)$_3$X (X = halogen), are known.[27]

D. EPR Spectra, Optical Transitions, and Electronic Structure. Octahedral low-spin d^5 complexes have the ground state $^2T_{2g}$ corresponding to the electronic configuration t_{2g}^5. The symmetry of Ru(meR)$_3$ is C_3 or lower.[24] In C_3 symmetry t_{2g} splits into a and e (consisting of the degenerate pair[28] e_+ and e_-) and $^2T_{2g}$ splits into ^2A and ^2E ($^2E_+$, $^2E_-$). In rhombic symmetry all orbital degeneracies must disappear. The axial and rhombic splitting parameters are designated Δ and V. When a lies above e (i.e. ^2E lies above ^2A) Δ is defined to be positive as in Figure 2. The EPR technique is ideally suited[29–36] for determining the sign and magnitude of Δ. The required formalism is briefly summarized elsewhere in this paper.

A representative EPR spectrum of Ru(meR)$_3$ measured in a frozen (77 K) 1:1 chloroform–toluene glass is shown in Figure 3. The three observed g values (g_1, g_2, and g_3 in order of decreasing magnitude)[37] are collected in Table IV. As a first approximation the spectra can be considered as axial with g_3 corresponding to the parallel resonance. The presence of a relatively weak rhombic distortion is apparent in the splitting of the perpendicular resonance into two closely spaced components (g_1 and g_2). Thus Ru(meR)$_3$ like the 3d tris(thiohydroxamato) complexes has only approximate C_3 symmetry.[24] Diamagnetic Co(mePh)$_3$ undergoes facile doping by Ru(mePh)$_3$. The powder EPR spectrum of the doped lattice at 77 K (Table IV) is a close analogue[38] of the frozen-solution spectrum.

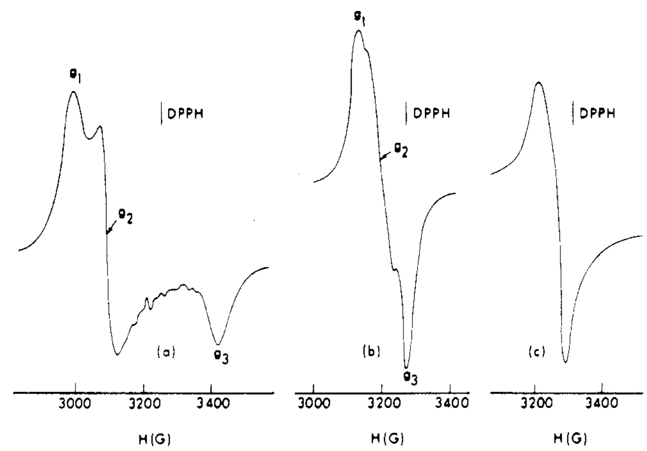

Figure 3. EPR spectra at 77 K of (a) [Ru(mePh)$_3$] in 1:1 chloroform–toluene, (b) Na[Ph$_4$As]$_2$[Ru(ph)$_3$]·H$_2$O in 1:1 acetonitrile–toluene, and (c) Ru(ph)$_3^-$ produced coulometrically in acetonitrile (0.1 M TEAP).

The EPR-active ground-state Kramers doublet can be written as in eq 3, where states with β spin are identified by putting a

$$\psi_a = p|E_+\rangle + q|\bar{A}\rangle + r|E_-\rangle$$
$$\psi_b = p|\bar{E}_-\rangle + q|A\rangle + r|\bar{E}_+\rangle \qquad (3)$$

bar on top. The experimental g factors afford values of the parameters k, p, q, r, Δ/λ, V/λ, ϵ_1/λ and ϵ_2/λ, where k is a fictitious orbital reduction factor,[39] ϵ_i's are the energy gaps among the three Kramers doublets and λ is the spin–orbit coupling constant. Identifying the pseudo-C_3 axis as the z axis, we write[40] $g_1 = |g_x|$, $g_2 = |g_y|$, and $g_3 = |g_z|$. The signs of the g components are not provided by the EPR experiment, and two alternative solutions differing in the sign of g_z are possible (solutions 1 and 2, Table V). The two solutions differ widely in the values of the various parameters. In particular we note the disparity of ϵ_1/λ and ϵ_2/λ in the two cases.

The choice between the two solutions can be made on the basis of energies of optical transitions among the Kramers doublets. Taking[41] $\lambda \sim 1000$ cm^{-1}, the energies of these crystal field transitions are predicted to be $\epsilon_1 \sim 7000$ cm^{-1} (1430 nm) and $\epsilon_2 \sim 5000$ cm^{-1} (2000 nm) in the case of solution 1. A relatively weak and broad band is indeed systematically observed in solutions[42] of all Ru(meR)$_3$ complexes at 1500 nm (Table I). This is not an overtone of any band occurring in the infrared, since Co(meR)$_3$ is completely transparent in this region. For most part the band is Gaussian in shape, but the observed absorption in the longer wavelength side is in excess and is suggestive of the presence

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(37) On the high-field side of g_2 and low-field side of g_3 a few weak resonances are systematically observed, which undoubtedly represent part of the hyperfine manifold of metal isotopes with magnetic nuclei (^{101}Ru, $I = {}^5/_2$; ^{99}Ru, $I = 3$; natural abundance 16.98% and 12.8%, respectively).
(38) The hyperfine splittings[37] are more clearly resolved in this case.
(39) Ideally the orbital reduction factor is a measure of covalency. However k, as determined from EPR analysis of the present type, acts as a "sink" for various unaccounted effects.[30,33] Reported values of k for pseudooctahedral ruthenium(III) complexes span the range[30–36] 0.4–1.2.
(40) If the identification of $|g_x|$ and $|g_y|$ is interchanged, merely the signs of V and r change and other parameters remain unchanged.
(41) The free-ion value of λ is 1100 cm^{-1}.[35] On complex formation there is a decrease[30–36] in the value of λ due to covalency.
(42) In acetonitrile solution spectra could be run upto 2200 nm while carbon tetrachloride is transparent to 2500 nm—the limit of the spectrophotometer used.

Table V. Assignments of g Values and Values of Parameters[a]

compd	soln no.	g_x	g_y	g_z	p	q	r	k	Δ/λ	V/λ	ϵ_1/λ	ϵ_2/λ
$Ru(mePh)_3$	1	-2.178	-2.109	1.907	0.136	0.990	0.018	0.475	5.655	-1.687	4.850	6.752
	2	-2.178	-2.109	-1.907	0.800	0.599	0.006	1.050	0.086	-0.026	1.473	1.531
$Ru(meAn)_3$	1	-2.175	-2.112	1.911	0.133	0.991	0.016	0.481	5.762	-1.598	4.992	6.818
	2	-2.175	-2.112	-1.911	0.800	0.599	0.006	1.050	0.084	-0.024	1.473	1.530
$Ru(meBz)_3$	1	-2.177	-2.110	1.913	0.132	0.991	0.018	0.485	5.850	-1.741	5.015	6.966
	2	-2.177	-2.110	-1.913	0.801	0.599	0.007	1.051	0.084	-0.026	1.473	1.530

[a] Symbols have the same meaning as in the text.

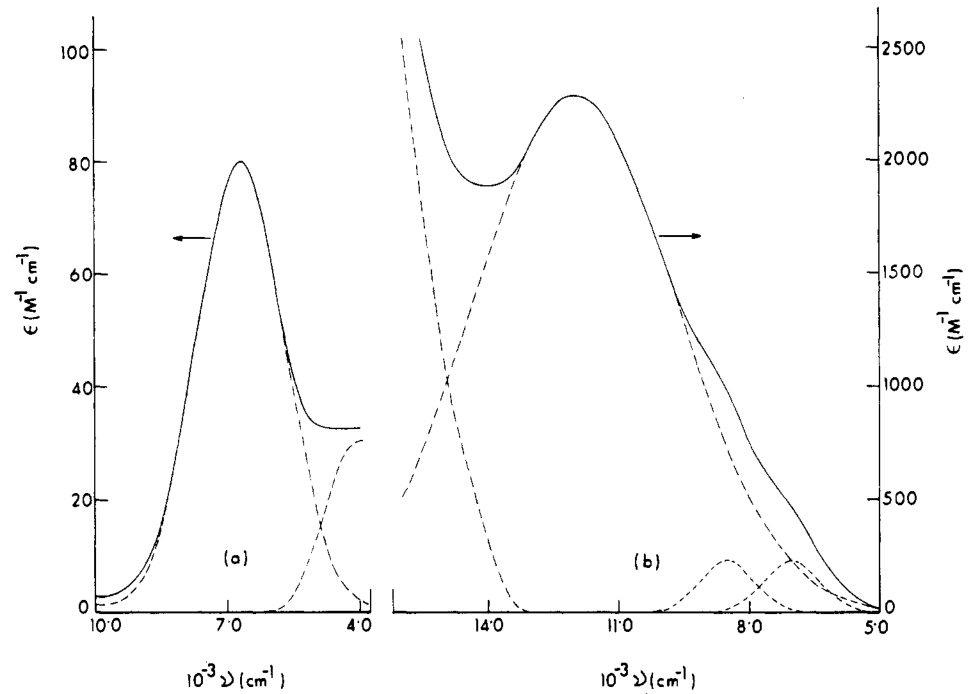

Figure 4. Experimental electronic bands (solid lines) and their Gaussian components (dotted lines) for (a) $[Ru(meAn)_3]$ in carbon tetrachloride and (b) $Na[Ph_4As]_2[Ru(ph)_3]\cdot H_2O$ in acetonitrile.

of additional transition(s) (Figure 4). The spectral results thus demonstrate that the ground state of the $Ru(meR)_3$ complexes is correctly represented by solution 1. This state is nearly pure A in character with only marginal mixing of E_+ and E_-. Like those of the ruthenium(III) tris complexes of some other sulfur donor ligands,[33] the k values of the present complexes are unusually low ($\sim$0.5).

We now consider solution 2. Here the transitions should occur around 1500 cm^{-1}. The nature of the infrared spectra of $M(meR)_3$ (M = Co, Fe, Ru), already discussed in an earlier section, eliminates this solution. Further it will be extremely difficult to explain the origin of the $\sim$7000-cm^{-1} band in terms of this solution. Thus $Ru(meR)_3$ represents a case of relatively large axial distortion associated with a significant rhombic component.

The $Ru(meR)_3^+$ complexes show a shoulder at 1200 nm superposed on an allowed band at $\sim$830 nm (Table I). This shoulder may correspond to one or more transitions of type $e^3a^1 \rightarrow e^2a^2$ within the t_2 shell. Since axial splitting would be larger in $Ru(meR)_3^+$ compared to that in $Ru(meR)_3$, the energy of transition(s) within the t_2 shell should be higher in the former, as observed. The $Ru(meR)_3^+$ species are EPR silent both at room temperature and at 77 K, probably due to rapid relaxation. This is not unusual for a d^4 system.

E. Tris(thiohydroximato) Complexes: Three Oxidation Levels. The concerned ligand is PhC(S)N(OH)H, abbreviated H_2ph, where both protons are potentially dissociable. Application of the procedure used for the synthesis of $Ru(meR)_3$ complexes did not afford tractable products in the case of the present ligand. However addition of sodium methoxide to the reaction mixture furnished the fully deprotonated red-violet anion $Ru^{III}(ph)_3^{3-}$ isolated as a mixed sodium tetraphenylarsonium salt. By cerium(IV) oxidation, the corresponding blue salt of the cation $Ru^{IV}(ph)_3^{2-}$ is obtained. These salts have the expected electrical conductivities and magnetic moments and show several optical transitions (Table I). We believe that the allowed electronic bands at 640, 840, 830, and 1075 nm in the cases of $Ru(mePh)_3$, $Ru(mePh)_3^+$, $Ru(ph)_3^{3-}$, and $Ru(ph)_3^{2-}$, respectively, correspond to one another and arise from ligand $\rightarrow$ metal change transfer. Shift to lower energies occurs on both metal oxidation and ligand demethylation as expected.

A facial stereochemistry (type **2**, z = −3, −2) like that[15] of $Cr(ph)_3^{3-}$ is probable for the complexes. While the ruthenium(IV) complex $Ru(ph)_3^{2-}$ is EPR silent as usual, the ruthenium(III) anion $Ru(ph)_3^{3-}$ shows three closely spaced g values (Figure 3; Table IV). Using the earlier correspondences among g_1, g_2, g_3 and g_x, g_y, g_z, we note that g_x and g_y lie above 2 while g_z is $\sim$2.0. Under such circumstances an analysis in terms of the crystal field model used in the last section is no longer meaningful.[33] Certain observations are, however, in order. If the geometric structures of $Ru(mePh)_3$ and $Ru(ph)_3^{3-}$ are similar,[43] the observed EPR results would require that the covalency and the anisotropy thereof are larger in $Ru(ph)_3^{3-}$ than those in $Ru(mePh)_3$. This is reasonable in view of the higher negative charge on the ligand in the former case. The net distortion reflected in the EPR parameters is the sum of geometrical distortion and anisotropy of covalent binding. In the limit of large net distortion,[33] g_x and g_y are expected to approach −2.0 and g_z should approach +2.0. The $Ru(ph)_3^{3-}$ ion appears to lie close to this situation. The electronic spectrum of $Ru(ph)_3^{3-}$ bears clear testimony to large distortion (Figure 4). The low-energy shoulders on the band having a maximum at 830

(43) We note that the geometric structures of $Cr(mePh)_3$ and $Cr(ph)_3^{3-}$ are closely similar as shown by X-ray work.[14,15] The same may very well be true for the ruthenium(III) complexes. This contention is based on the observed isomorphism of $Co(mePh)_3$ (which is isostructural[14] with $Cr(mePh)_3$) and $Ru(mePh)_3$.

nm can be neatly resolved into two relatively weak Gaussian components (1430 and 1180 nm). We believe that these represent the two transitions within the t_2 shell. Their energies are higher than those of the corresponding transitions in $Ru(meR)_3$, reflecting the larger splitting between a and e levels in $Ru(ph)_3^{3-}$.

The cyclic voltammogram of $Ru(ph)_3^{3-}$ shows three quasi-reversible (ΔE_p, 80–100 mV) one-electron responses (Figure 1; Table II). The same voltammogram can be generated by starting from $Ru(ph)_3^{2-}$. The responses having $E°_{298}$ of −0.16 and −1.17 V are assigned to couples 4 and 5, respectively. The formal potentials

$$Ru^{IV}(ph)_3^{2-} + e^- \rightleftharpoons Ru^{III}(ph)_3^{3-} \quad (4)$$

$$Ru^{III}(ph)_3^{3-} + e^- \rightleftharpoons Ru^{II}(ph)_3^{4-} \quad (5)$$

of these couples are thus significantly lower than those of the corresponding hydroxamate couples 1 and 2 (Table II). This phenomenon is of general applicability[3,4,6] and originates from the accumulation of an extra negative charge on each ligand in the case of hydroximates. Coulometrically produced solutions of $Ru(ph)_3^{4-}$ and $Ru(ph)_3^-$ are respectively brown and deep blue in color. Both are too unstable for isolation as pure salts.

The couple at 0.62 V, formally written as (6), is of considerable interest with regard to the oxidation state of $Ru(ph)_3^-$. Two

$$Ru(ph)_3^- + e^- \rightleftharpoons Ru^{IV}(ph)_3^{2-} \quad (6)$$

alternative formal descriptions are possible: (1) a ruthenium(IV)-stabilized ligand radical[44] description, $Ru^{IV}(ph)_2(ph\cdot)^-$; (2) a ruthenium(V) description, $Ru^V(ph)_3^-$. Either way $Ru(ph)_3^-$ represents an uncommon situation. To our knowledge no examples of the former description exist in the literature. On the other hand, few genuine ruthenium(V) complexes are known and those reported[45,46] invariably have F^- or O^{2-} as at least one of the ligands. An attempt was made to choose between the two alternatives by using EPR spectra.

On constant potential coulometric oxidation (at 0.2 V) of $Ru(ph)_3^{3-}$ in acetonitrile, the original EPR signal disappears due to the formation of EPR-silent $Ru(ph)_3^{2-}$. The solution is then oxidized further at 0.75 V after the solution temperature is lowered to 278 K (to ensure better stability to the $Ru(ph)_3^-$ formed). When a Coulomb count corresponding to the transfer of one electron is accumulated, the deep blue solution of $Ru(ph)_3^-$ was immediately frozen to 77 K. The solution is EPR active. A slightly asymmetric signal at $g \sim 2$ is all that is observed (Figure 3). The low-field and high-field turning points of the signal are separated by ~125 G.

We scrutinize the $Ru^V(ph)_3^-$ description first. Here the metal ion has a d^3 configuration. Depending on the extent of zero-field splitting, the EPR spectra of pseudooctahedral d^3 ions in frozen solution can take various forms.[47] In the limit of small splitting ($D << h\nu$, $h\nu = 0.31$ cm^{-1} at X-band) a single dominating $g \sim 2$ signal[48] is expected as in the cases of tris(dithiocarbamato) complexes of chromium(III),[49] manganese(IV),[50] and some other species.[47] Comparisons[51] with $Cr(mePh)_3$, $Cr(ph)_3^{3-}$, and $Mn(mePh)_3^+$ are probably more relevant. While the chromium(III) complexes have EPR spectra ($g \sim 4$ and 2) characteristic of moderate zero-field splitting, such splitting is small ($D < 0.01$ cm^{-1}) in the manganese(IV) complex whose predominant signal is[51] at $g \sim 2$. It is therefore not untenable to consider $Ru(ph)_3^-$ as a ruthenium(V) complex with small zero-field splitting although the smallness of the splitting is puzzling in view of the large distortion (vide supra) in $Ru(ph)_3^{3-}$.

If $Ru(ph)_3^-$ is considered as $Ru^{IV}(ph)_2(ph\cdot)^-$ we have the case of a ligand radical bound to a rapidly relaxing transition-metal ion, viz. ruthenium(IV). Here a broad radical signal can arise[52] provided the spin exchange interaction between the radical and the metal ion is not excessive. Otherwise no signal may be observable. The EPR spectrum of $Ru(ph)_3^-$ therefore does not as such exclude the ligand radical description either. However the lack of strong exchange between metal and ligand spins would be difficult to understand since the two entities are bonded so closely (see also ref 44).

While the state of oxidation of $Ru(ph)_3^-$ remains uncertain,[53] the $Ru^V(ph)_3^-$ description appears to have an edge over the $Ru^{IV}(ph)_2(ph\cdot)^-$ description.

F. Concluding Remarks. For hydroxamates and hydroximates the reported[3,4] ruthenium complexes have unsaturated nitrogenous ligands such as 2,2′-bipyridine or 2-arylazopyridine as coligands, and authentic tris chelates have not been obtainable so far. In contrast the thiohydroxamates and thiohydroximates afford tris chelates quite readily with both ruthenium(III) and ruthenium(IV). The ruthenium(II) congeners can be produced coulometrically in solution, but these have not been isolated in the pure state. The formal potentials of the couples connecting the various oxidation states are generally low. In the case of thiohydroxamates the ruthenium(IV)–ruthenium(III) potential is only ~0.3 V—a value that is comparable to that of tris(dithiocarbamato) complexes.[27] In the thiohydroximate case this potential drops to −0.16 V—the lowest value reported so far. In this case the oxidation level can be advanced further by an one-electron step, but the site (metal or ligand) of ionization remains uncertain although the metal site (formation of ruthenium(V)) seems more probable. The hydroximate ligand appears to be able to span all oxidation states of ruthenium from +2 to +5.

The ruthenium(III) species have facial stereochemistry characterized by relatively large distortions, which are consistently reflected in EPR and optical spectra. The sign of the axial parameter Δ is positive corresponding to the a > e order within the split t_2 shell. We have recently examined[51] the EPR spectra of a sizeable number of tris chelates of ruthenium(III) derived from unsaturated N,O-donors. These also have large and positive Δ. The recurrence of this feature among ruthenium(III) tris chelates is indeed striking, and the existence of a possible common ground for this effect is under scrutiny.

We conclude by stating an observation that has not been recorded in the preceding text. On prolonged storage $Ru(meR)_3$ is converted into a red product apparently without any change in elemental composition. This transformation can be hastened by heating. Experiments performed on the meAn case show that the red product is diamagnetic and displays four successive quasi-reversible one-electron couples (−1.13, −0.55, 0.84, and 1.05 V). The red complex appears to be a magnetically coupled ruthenium(III)–ruthenium(III) dimer. Its nature is under scrutiny.

Experimental Section

Materials. The purification of solvents and preparation of supporting electrolytes for electrochemical works were done as before.[6] Grignard reagents were made by the literature method.[54] Dinitrogen gas was purified by bubbling it through an alkaline dithionite reducing solution. Cerium(IV) solutions were prepared from reagent grade ceric ammonium

(44) That the ligand is oxidizable can be demonstrated by voltammetry of the complex[10] $Zn(ph)_2^{2-}$. A highly irreversible oxidation is seen in dimethylformamide at ~0.7 V. This oxidation must be localized on the ligand since the metal ion is nonoxidizable in solution. The detailed nature of this oxidation is unknown since the oxidized complex decomposes immediately. We note that in combination with a metal(IV) ion, ligand oxidation should occur considerably above 0.7 V while the formal potential of couple 6 is 0.62 V.

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sulfate. Purification of $RuCl_3 \cdot 3H_2O$ was done as previously recorded.[55] All other chemicals used for the preparative works were of reagent grade and were used without further purification.

Physical Measurements. Electronic and infrared spectra were recorded on Hitachi 330 and Perkin-Elmer 783 spectrophotometers, respectively. Solution electrical conductivity was measured by using a Philips PR 9500 bridge with a solute concentration of $\sim 10^{-3}$ M. Control of solution pH where required in synthetic work was achieved by using a Systronics Model 335 pH meter. Magnetic moments were measured with the help of a PAR 155 vibrating sample magnetometer. Cyclic voltammetry was performed under a dinitrogen atmosphere with the help of PAR Model 370-4 electrochemistry system as before.[6] In three-electrode configuration, a Beckman Model 39273 platinum electrode was the working electrode. For controlled potential coulometry a PAR Model 173 potentiostat, Model 179 digital coulometer and Model 377A cell system having a platinum wire gauge electrode were used. All measurements were made at 298 K. The potentials are referenced to a saturated calomel electrode and are uncorrected for junction potential. EPR measurements were made with a Varian 109C E-line X-band spectrometer using a quartz Dewar. All spectra were calibrated with the help of DPPH ($g = 2.0037$). Microwave power level was maintained at around 0.2 mW. Powder photographs were taken in a Phillips Debye–Scherrer camera (diameter 11.54 cm) using Cu Kα radiation (Ni filtered). The film was appropriately shielded to minimize the fluorescence background in the case of $Co(mePh)_3$.

Analysis of EPR Data. The procedure of Hill,[30] which takes all five (t_2^5) electrons into explicit consideration, was followed. The three one-electron t_2 functions were written[28] in terms of spherical harmonics. The ^2A and ^2E (consisting of $^2E_+$ and $^2E_-$) states for the axial case are obtained by populating these functions with five electrons. In the rhombic case the E representation is no longer appropriate. However the E_+ and E_- labels are still used to stress the parenthood of the states so labeled. The effect of Δ, V, and λ is to split the six $^2T_2$ functions into three Kramers doublets represented by two identical 3×3 matrices

$$\begin{array}{ll|ccc} & & |E_-\rangle & |\bar{A}\rangle & |E_+\rangle \\ & & |\bar{E}_+\rangle & |A\rangle & |\bar{E}_-\rangle \\ \hline |E_-\rangle & |\bar{E}_+\rangle & 2\Delta + \lambda/2 & 0 & V/2 \\ |\bar{A}\rangle & |A\rangle & 0 & \Delta & -\lambda/\sqrt{2} \\ |E_+\rangle & |\bar{E}_-\rangle & V/2 & -\lambda/\sqrt{2} & 2\Delta - \lambda/2 \end{array} \quad (7)$$

The three components of the **g** tensor are

$$g_x = 2[-2pr - q^2 - 2^{1/2}kq(p + r)] \quad (8)$$

$$g_y = 2[2pr - q^2 - 2^{1/2}kq(p - r)] \quad (9)$$

$$g_z = 2[-p^2 + q^2 - r^2 - k(p^2 - r^2)] \quad (10)$$

where p, q, and r are as in eq 3 and k is the orbital reduction factor.[39] The normalization condition for coefficients is given by

$$p^2 + q^2 + r^2 = 1 \quad (11)$$

Changing the signs of any two of the equations among eq 8–10 corresponds to a mere rotation by π rad around an axis and leaves the physical results unaffected.[56] The signs as chosen in eq 8–10 afford identical (in sign and magnitude) g_x and g_y in the axial case ($r = 0$). Experimental g values afforded the p, q, r, and k parameters, which were used to solve appropriate secular equations of Δ, V, and the energy of the ground Kramers doublet (in units of λ). The energies of all three Kramers doublets were extracted by diagonalizing the matrix in eq 7. Standard computational methods[31] were used. A program was written suitable for a Burroughs 6700 computer.

Gaussian Analysis of Bands. The Gaussian function was used in the form[57] of eq 12 (where ϵ_ν and ϵ_0 are the extinction coefficients at frequency ν and at band maximum ν_0, respectively and δ is the full width at half height). Fitting was done by trial and error.

$$\epsilon_\nu = \epsilon_0 \exp\left[\frac{-5.545(\nu - \nu_0)^2}{2\delta^2}\right] \quad (12)$$

Synthesis of Compounds. Thiohydroxamic acids were prepared from appropriate carboxymethyl dithio esters[58] and hydroxylamine or N-methylhydroxylamine by using a literature procedure.[23] $Cr(mePh)_3$, $Cr(ph)_3^{3-}$, $Co(mePh)_3$, and $Zn(ph)_2^{2-}$ were prepared by using a reported method.[10,11,15]

The synthesis of $Ru(meR)_3$ and $Ru(meR)_3ClO_4 \cdot H_2O$ was performed by using a general method. Specific details are given for one representative example in each case.

Tris(*N*-methyl-*p*-methoxybenzothiohydroxamato)ruthenium(III), Ru(*p*-OMeC$_6$H$_4$C(S)N(Me)O)$_3$. To a solution of 480 mg (2.44 mmol) of *N*-methyl-*p*-methoxybenzothiohydroxamic acid in 10 mL of ethanol was added 200 mg (0.76 mmol) of $RuCl_3 \cdot 3H_2O$ dissolved in 40 mL of water. Dilute sodium hydroxide was allowed to run into the solution with stirring until the pH becomes 3.5. The green precipitate separated from the solution was collected by filtration and washed thoroughly by cold water and finally with solvent ether to remove the ligand, if any, mixed with the crude product. The solid was dried in vacuo over P_4O_{10}.

The crude dried product was dissolved in a small volume of dichloromethane and was subjected to chromatography on a neutral alumina column (20 × 1 cm). On elution with benzene–acetonitrile (3:2), a small light brown band moved out very fast and was rejected. A slower moving deep green band was eluted out by using the same solvent mixture but with a changed volume ratio (2:3). A dark brown band remained near the top of the column. On slow evaporation of the eluant, the desired complex was obtained in crystalline form. Yield: 60%. Anal. Calcd for $Ru(C_9H_{10}NO_2S)_3$: C, 47.02; H, 4.35; N, 6.09. Found: C, 46.70; H, 4.40; N, 5.90.

Tris(*N*-methylbenzothiohydroxamato)ruthenium(III), Ru(C$_8$H$_8$NOS)$_3$. Anal. Calcd: C, 48.07; H, 4.01; N, 7.01. Found: C, 47.95; H, 3.95; N, 7.50.

Tris(*N*-methylphenylacetothiohydroxamato)ruthenium(III), Ru(C$_9$H$_{10}$NOS)$_3$. Anal. Calcd: C, 50.54; H, 4.68; N, 6.55. Found: C, 50.50; H, 4.60; N, 6.40.

Tris(*N*-methyl-*p*-methoxybenzothiohydroxamato)ruthenium(IV) Perchlorate Monohydrate, Ru(*p*-OMeC$_6$H$_4$C(S)N(Me)O)$_3$ClO$_4$·H$_2$O. To a solution of 90 mg (0.13 mmol) of pure $Ru(p\text{-}OMeC_6H_4C(S)N(Me)O)_3$ in 30 mL of acetonitrile was added 120 mg (0.19 mmol) of ceric ammonium sulfate dissolved in 20 mL of 1 M perchloric acid. The reaction mixture was filtered and reduced to 10 mL in a vacuum evaporator. The dark pink complex was separated by filtration and washed throughly with cold water. The mass was dried over P_4O_{10}. The oxidation can be carried out in neutral ceric solution, but it takes a long time to complete the reaction. The crude product was dissolved in a minimum volume of acetonitrile and was subjected to chromatography on a silica gel (60–120 mesh) column (20 × 1 cm). On elution with benzene–acetonitrile (4:1) a pink-red band moved out very fast and was collected. A bluish green band remained near the top of the column. The required complex was obtained from the eluant in crystalline form by slow evaporation. Yield: 75%. Anal. Calcd for $Ru(C_9H_{10}NO_2S)_3ClO_4 \cdot H_2O$: C, 40.17; H, 3.97; N, 5.21. Found: C, 40.35; H, 3.95; N, 5.15.

Tris(*N*-methylbenzothiohydroxamato)ruthenium(IV) Perchlorate Monohydrate, Ru(C$_8$H$_8$NOS)$_3$ClO$_4$·H$_2$O. Anal. Calcd: C, 40.19; H, 3.63; N, 5.86. Found: C, 40.01; H, 3.57; N, 5.78.

Tris(*N*-methylphenylacetothiohydroxamato)ruthenium(IV) Perchlorate Monohydrate, Ru(C$_9$H$_{10}$NOS)$_3$ClO$_4$·H$_2$O. Anal. Calcd: C, 42.71; H, 4.22; N, 5.54. Found: C, 42.85; H, 4.31; N, 5.62.

The synthesis of the thiohydroximato complexes was achieved as follows.

Sodium Bis(tetraphenylarsonium) Tris(benzothiohydroximato)ruthenate(III) Monohydrate, Na[Ph$_4$As]$_2$Ru(C$_6$H$_5$C(S)NO)$_3$·H$_2$O. A solution of 200 mg (0.76 mmol) of $RuCl_3 \cdot 3H_2O$ in 20 mL of water was added with stirring to a solution of 450 mg (2.94 mmol) of benzothiohydroxamic acid in 30 mL of ethanol. To the dark green solution thus produced was added dropwise 2 gm of NaOMe in 15 mL of ethanol. Addition should be completed within 15 min. Excess Ph_4AsCl ($\sim$3 g) in 10 mL of water was added, and stirring was continued for another 5 min. The reaction mixture was filtered, and the volume of the filtrate was brought to 25 mL. The separated pink-red solid was thoroughly washed with water and dried in vacuo over P_4O_{10}. The dried mass was recrystallized from dichloromethane–hexane; yield 40%. Anal. Calcd for $Na((C_6H_5)_4As)_2Ru(C_6H_5C(S)NO)_3 \cdot H_2O$: C, 60.84; H, 4.19; N, 3.09. Found: C, 60.47; H, 4.10; N, 3.14.

Sodium Tetraphenylarsonium Tris(benzothiohydroximato)ruthenate(IV) Monohydrate, Na[Ph$_4$As]Ru(C$_6$H$_5$C(S)NO)$_3$·H$_2$O. To a solution of 200 mg (0.15 mmol) of $(Ph_4As)_2NaRu(C_6H_5C(S)NO)_3 \cdot H_2O$ in 20 mL of acetonitrile was added dropwise a solution of 110 mg (0.17 mmol) of ceric ammonium sulfonate in 20 mL of water. The mixture was filtered immediately, and the organic solvent was removed under reduced pressure. The dark blue solid that separated from the solution was collected

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by filtration, washed with cold water, and dried over P_4O_{10} in vacuo. The compound was recrystallized from cold dichloromethane–hexane; yield 80%. Anal. Calcd for $Na((C_6H_5)_4As)Ru(C_6H_5C(S)NO)_3 \cdot H_2O$: C, 55.21; H, 3.78; N, 4.29. Found: C, 55.10; H, 3.80; N, 4.37.

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Registry No. Ru(mePh)$_3$, 97751-77-4; Ru(meAn)$_3$, 97751-78-5; Ru(MeBz)$_3$, 97751-79-6; [Ru(mePh)$_3$]ClO$_4$, 97751-81-0; [Ru(meAn)$_3$]ClO$_4$, 97751-83-2; [Ru(meBz)$_3$]ClO$_4$, 97751-85-4; Na[Ph$_4$As]$_2$[Ru(ph)$_3$], 97751-87-6; Na[Ph$_4$As][Ru(ph)$_3$], 97751-89-8; Ru(mePh)$_3^-$, 97751-90-1; Ru(meAn)$_3^-$, 97751-91-2; Ru(meBz)$_3^-$, 97751-92-3; Ru(ph)$_3^{4-}$, 97751-93-4.

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Active-Site Chemistry of Hemerythrin: Kinetic Studies on the Reduction of the Met Octamer Form from *Themiste zostericola* with $[Co(sep)]^{2+}$, $[Co(sarCl_2)]^{2+}$, $[Co(9\text{-aneN}_3)_2]^{2+}$, and $[Cr(bpy)_3]^{2+}$

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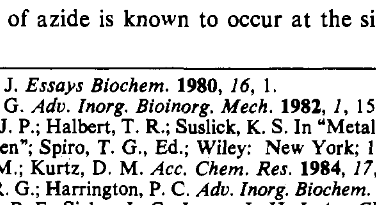
The kinetics of reduction of the binuclear Fe(III,III) active site in the octameric metHr from *Themiste zostericola* through to the Fe(II,II) deoxy form by 1-equiv reductants $[Co(sep)]^{2+}$, $[Co(sarCl_2)]^{2+}$, $[Co(9\text{-aneN}_3)_2]^{2+}$, and $[Cr(bpy)_3]^{2+}$ have been studied at 25 °C, $I = 0.15$ M (Na_2SO_4). Three stages are observed, which require ~12 h to proceed to completion. The stopped-flow first stage conforms to a rate law first order in both reactants, with rate constants (k_1/M^{-1} s^{-1}) for $[Co(sep)]^{2+}$ (255), $[Co(sarCl_2)]^{2+}$ (114), $[Co(9\text{-aneN}_3)_2]^{2+}$ (12.8), and $[Cr(bpy)_3]^{2+}$ (2.5×10^5). Uniphasic kinetics are observed over the pH range 6.3–9.0, indicating that the reaction is insensitive as to whether hydroxomet (formed in a slow process pK_a ~ 8) is present or not. The pH dependences of k_1 indicate an additional (fast) pK_a of 7.6. Rate constants k_{2obsd} for the second stage (2.0×10^{-3} s^{-1} at pH 6.3) are independent of the concentration and identity of the reductant, and give a pK_a close to that for k_1. The third stage k_{3obsd} (1.2×10^{-4} s^{-1}) is independent of reductant and pH. With dithionite as reductant, the same k_{2obsd} and k_{3obsd} values are obtained. It has been demonstrated that 8, 4, and (by inference) 4 equiv of reductant, respectively, are consumed in each of the three stages required for complete reduction of the octamer. It is concluded that the Fe(II,III) units present in the semi-met form at the end of the first stage have a structure different from the four remaining in the quarter-met at the end of the second stage. Strong reductants $[Cr(edta)]^{2-}$ and dithionite were also used to generate UV–vis spectra of intermediate states.

Introduction

Hemerythrin is one of three naturally occurring O_2 carriers.[1-5] It is found in four different invertebrate phyla, the sipunculids, brachiopods, polychaetes, and priapulids, of which the former are the major source and the most extensively studied. Hemerythrin for this work was obtained from the spinuculid marine worm *Themiste zostericola*. The octamer (mol wt 108 000) obtained from the erythrocytes consists of eight identical subunits each of which has a binuclear Fe non-heme active site. Little or no cooperativity is observed for the extracted octamer, and the reason for its existence in this state is not at present understood. A monomer has also been isolated from the retractor muscle and will be the subject of further studies.

Recent X-ray studies on crystals of Fe(III,III) methemerythrin from *Themiste dyscritum* (pH ≤6.5) have indicated a structure in which one of the Fe(III) atoms is octahedral and the other is trigonal bipyramidal:[6]



Coordination of azide is known to occur at the sixth (vacant) position, and O_2 is believed to bind to the deoxy form, Fe(II,II), at this same site giving a product that can be described as peroxo Fe(III,III). It has recently been demonstrated that OH^- coordinates to the 5-coordinate Fe of the met form in a slow acid–base equilibrium,[7,8] the pK_a of which is 7.8 for *Phascolopsis gouldii* and 8.4 for *Themiste dyscritum*. Similar reactivity is observed for the met form from *Themiste zostericola*. EXAFS,[9] Mössbauer,[10] and resonance Raman[11] studies support a μ-oxo-bridged structure for both met and oxy forms, and structural features include Fe–O(oxo) (*ca.* 1.75 Å) and Fe–Fe (ca. 3.3 Å) bonds and an Fe–O–Fe angle of 165°. In the deoxy form the two Fe(II)'s are not coupled antiferromagnetically,[10,12] and EXAFS studies suggest that there is no μ-oxo bridge.[9] This question is also addressed by Reem and Solomon.[13]

In order to better understand the chemistry of the hemerythrin active site, which is now believed to function also in purple acid phosphatase[14] and ribonuclease,[15] we have commenced a program of study in which redox interconversions are investigated in more detail. Wilkins and colleagues have studied previously the reduction of metHr with dithionite[16] and have successfully characterized by EPR a semi-met intermediate.[17] Other studies by

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