Chemistry of Ruthenium. Part 4.† *trans*-Dihalogeno(isonitrosoketone)-(isonitrosoketonato)ruthenium(III). Structure and Stability, Electron Spin Resonance, Electron Transfer, and Proton Transfer

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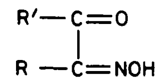
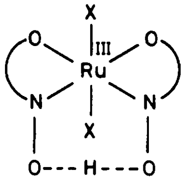
A group of ruthenium(III) complexes of type $[RuX_2(HL)(L)]$ is reported [HL = R′C(=O)C(=NOH)R; X = Cl or Br]. The RuX_2 group is *trans* and the hydrogen-bonded (HL)(L) moiety acts as a planar tetradentate chelator. The low CO stretching frequencies and better stability of R′ = Ph *versus* R′ = Me species are rationalised in terms of ionic resonance. The complexes display ligand to metal charge-transfer (l.m.c.t.) transitions at relatively low energies (500—800 nm). They are uniformly low-spin ($S = \frac{1}{2}$) and have axial e.s.r. spectra. The *g* parameters ($g_{\parallel}$ *ca.* 1.86, $g_{\perp}$ *ca.* 2.50) are used to compute tetragonality (Δ), orbital reduction (*k*), and other parameters within the basic framework of crystal-field theory. The *d*-orbital order d_{xz}, $d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$ with the hole in d_{xy} is indicated. The possible role of l.m.c.t. contribution in making both *k* and $g_{\parallel}$ large is discussed. $[RuX_2(HL)(L)]$ undergoes a reversible one-electron electrochemical reduction to blue $[RuX_2(HL)(L)]^-$. This species can also be generated chemically. The redox process has been thoroughly studied using cyclic voltammetry and phase-sensitive alternating current voltammetry. Formal potential (*ca.* 0.4 V), diffusion coefficient, and heterogeneous rate-constant data are presented. Addition of NEt_3 deprotonates $[RuX_2(HL)(L)]$ to $[RuX_2L_2]^-$. Reprotonation occurs on adding $HClO_4$. Deprotonation dramatically affects the electrochemical response. In this context the symbiotic relationship between electron transfer and proton transfer is noted.

WHILE oximes have an extensive chelate chemistry,[1] relatively little is known [2,3] about the oximates of ruthenium. The present work is a part of our systematic studies [4-6] in this area. The ligands studied here are isonitrosoketones (hydroxyiminoketones), –C(=O)–C(=NOH)–. Well characterised metal complexes of isonitrosoketones are sparse.[1] In a few cases, however, it has been demonstrated from *X*-ray work [2,7,8] that such ligands chelate metal ions *via* oxime-N and carbonyl-O atoms. Apart from the tris(violurato)ruthenium(II) anion and related species [2] nothing is known about the ruthenium chemistry of isonitrosoketones. The ligands (1) of the present study are abbreviated as HL [1-5]; one species, $[RuX_2(HL^3)(L^3)]$ [X = Cl or Br], has been shown [5] to have a structure of type (2). The synthetic reaction has now been extended to other ligands (HL) in order to observe the effect of R and R′ substituents. The main purpose of this investigation is to make a rational study of relative stability, charge-transfer spectra, electron spin resonance spectra, electron-transfer reactions, and proton-transfer reactions in the related group of $[RuX_2(HL)(L)]$ species.



	R′	R
HL^1	Ph	H
HL^2	Ph	Me
HL^3	Ph	Ph
HL^4	Me	Me
HL^5	Me	Ph

(1)



(2)

EXPERIMENTAL

Chemicals and Starting Materials.—Hydroxyiminopropiophenone (HL^2), α-benzil oxime (HL^3), biacetyl oxime (HL^4), and α-hydroxyimino-α-phenylacetone (HL^5) were prepared using reported methods.[9-11] The preparation of hydroxyiminoacetophenone (HL^1) was similar to that of HL^2. $RuCl_3 \cdot 3H_2O$ was purified as described earlier.[5] Electrochemically pure acetonitrile and tetraethylammonium perchlorate were prepared as described previously.[5] Dichloromethane for electrochemical work was prepared from the commercial solvent by treatment with $NaHCO_3$ and anhydrous $CaCl_2$. Triethylamine was freshly distilled over KOH pellets before use. For deprotonation experiments, a solution of triethylamine of known concentration was prepared by directly adding a known weight of the amine to CH_3CN. Standard perchloric acid solution (*ca.* 0.01 mol dm^{-3} in CH_3CN) was prepared by adding a known amount of standardised concentrated (70% in aqueous solution) acid to CH_3CN.

Measurements.—Solution electrical conductivity was measured in acetonitrile using a Philips PR 9500 bridge with solute concentration of *ca.* 10^{-3} mol dm^{-3}. Electronic spectra were obtained from a Cary 17D spectrometer and i.r. spectra were recorded in KBr (4 000—400 cm^{-1}) and polyethylene discs (400—100 cm^{-1}) using Beckman IR-20A and IR-720 spectrometers respectively. Magnetic susceptibility was measured in a Gouy balance using $Hg[Co(SCN)_4]$ as a standard. E.s.r. spectra were recorded at the *X*-band with a JEOL-3X100 spectrometer fitted with a liquid-nitrogen cryostat. Electrochemical data were collected with the help of a Princeton Applied Research (PAR) 370-4 electrochemistry system as described previously.[5] Phase-sensitive studies were done using PAR M-124A lock-in amplifier, PAR M-372 polarography interface, and PAR M-174A polarographic analyser. Planar Beckman model 39273 platinum inlay working electrode, platinum wire auxiliary electrode, and a saturated calomel reference electrode (s.c.e.) were used in three electrode measurements and a platinum wire-gauge working electrode was used in coulometric experiments. Coulometric data are averages of at least three independent measurements. All electrochemical data were

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† Part 3 is ref. 6.

collected at 298 K and are uncorrected for junction potentials.

The area of the electrode (0.184 ± 0.001 cm^2) was determined chronoamperometrically.[12,13] Aqueous $K_4[Fe(CN)_6]\cdot 3H_2O$ ($D = 6.58 \times 10^{-6}$ cm^2 s^{-1}) in 0.1 mol dm^{-3} KCl was used as the standard. With the electrode area known, the diffusion coefficients D of the complexes were calculated using standard methods. The heterogeneous rate constant ($k_{s,h}$) was then derived by the method of Nicholson.[14]

Treatment of E.S.R. Data.—The crystal-field theory [15] of g tensors of low-spin d^5 systems in a distorted octahedral environment has been applied [15–20] to a number of systems. In axial cases the variables are the spin–orbit coupling constant (λ), the axial distortion parameter (Δ), and the orbital reduction factor (k). Using hole formalism the three spatial functions of the $^2T_2$ state are (1)—(3). In

$$|1\rangle = -(1/\sqrt{2})|d_{xz} + id_{yz}\rangle \qquad (1)$$

$$|-1\rangle = (1/\sqrt{2})|d_{xz} - id_{yz}\rangle \qquad (2)$$

$$|\zeta_1\rangle = id_{xy} = (1/\sqrt{2})\{|2\rangle - |-2\rangle\} \qquad (3)$$

general the ground Kramers doublet in an axial case can be represented by (4) and (5), where $\psi' = i\psi^*$; the g values are given by equations (6)—(8). While comparing our results

$$\psi = A|1^+\rangle + B|\zeta_1^-\rangle \qquad (4)$$

$$\psi' = A|-1^-\rangle - B|\zeta_1^+\rangle \qquad (5)$$

$$g_\perp = -2[B^2 + \sqrt{2}\,kAB] \qquad (6)$$

$$g_\parallel = 2[B^2 - (k + 1)A^2] \qquad (7)$$

$$A^2 + B^2 = 1 \qquad (8)$$

with those of others, *all reported* g *values are transformed so as to conform to the sign conventions* [19] of equations (6) and (7). Experimental g parameters yielded A, B, and k values [equations (6)—(8)]. These were used to solve the secular equations (9) and (10) for Δ and E in terms of λ. Usual computational methods [16] were used. The k interval was usually but not necessarily set as $0.5 \leqslant k \leqslant 2.0$.

$$[(\lambda/2) - E]A + (\lambda/\sqrt{2})B = 0 \qquad (9)$$

$$(\lambda/\sqrt{2})A + (\Delta - E)B = 0 \qquad (10)$$

Syntheses of Compounds.—The preparation of $[RuX_2(HL^3)(L^3)]$ [X = Cl, 2d; Br, 2e) has been reported earlier.[5] Details of the syntheses of other compounds are given below.

Dibromo(hydroxyiminoacetophenone)(hydroxyiminoacetophenonato)ruthenium(III) (2a).—$RuCl_3\cdot 3H_2O$ (260 mg, 1 mmol) was stirred magnetically for 10 min with LiBr (1 g) in ethanol (20 cm^3). To this mixture was added the ligand HL^1 (300 mg, 2 mmol) and 0.1 cm^3 concentrated perchloric acid. The mixture was warmed to 50 °C and stirring was continued for 15 min. It was then cooled to room temperature (25 °C) and kept in air for slow evaporation. The shining brown crystals were collected by filtration and were washed thoroughly with water and diethyl ether. The product was dried *in vacuo* over P_4O_{10} (yield *ca.* 60%) (Found: C, 33.8; H, 2.5; N, 5.0. Calc. for $C_{16}H_{13}Br_2N_2O_4Ru$: C, 34.4; H, 2.3; N, 5.0%).

Dichloro(α-hydroxyiminopropiophenone)(α-hydroxyiminopropiophenonato)ruthenium(III) (2b).—$RuCl_3\cdot 3H_2O$ (260 mg, 1 mmol) was stirred magnetically with LiCl (1 g) and HL^2 (330 mg, 2 mmol) in ethanol (20 cm^3) for 2 h at 50 °C. The colour of the solution changed from brown to deep red. It was then cooled to 0 °C and the precipitated compound was collected by filtration, and washed thoroughly with water and diethyl ether. The compound thus obtained was dried *in vacuo* over P_4O_{10} and was then dissolved in a small volume (5 cm^3) of CH_2Cl_2. This solution was subjected to chromatography on a silica gel column (30 × 1 cm) using benzene as eluant. A red band was eluted out. Crystallisation was done by adding hexane to the benzene eluate at room temperature (yield *ca.* 40%). Crystals are brown (Found: C, 43.2; H, 3.4; Cl, 14.2; N, 5.5. Calc. for $C_{18}H_{17}Cl_2N_2O_4Ru$: C, 43.5; H, 3.4; Cl, 14.3; N, 5.6%).

Dibromo(α-hydroxyiminopropiophenone)(α-hydroxyiminopropiophenonato)ruthenium(III) (2c).—This was prepared by the same procedure as above except that $RuCl_3\cdot 3H_2O$ was stirred for 10 min with 1 g LiBr (no LiCl was added) in ethanol (20 cm^3) prior to the addition of HL^2. Brown crystals were obtained (yield *ca.* 50%) (Found: C, 37.0; H, 3.4; N, 4.9. Calc. for $C_{18}H_{17}Br_2N_2O_4Ru$: C, 36.9; H, 2.9; N, 4.8%).

Reaction of $RuCl_3\cdot 3H_2O$ *with α-Hydroxyimino-α-phenylacetone* (HL^5).—$RuCl_3\cdot 3H_2O$ (260 mg, 1 mmol) in EtOH (20 cm^3) was stirred magnetically with LiCl (1 g) for 10 min. To this mixture was added HL^5 (330 mg, 2 mmol) and 0.1 cm^3 concentrated perchloric acid (if perchloric acid is not added, the solution rapidly turns blue and no crystalline mass could be isolated). The mixture was warmed to 50 °C and stirring was continued for 15 min. It was then cooled to room temperature (25 °C) and kept in air for slow evaporation. The precipitated complex was collected by filtration, washed with water and diethyl ether, and dried *in vacuo* over P_4O_{10}. The complex was chromatographed on a silica column following the procedure used for $[RuCl_2(HL^2)(L^2)]$. The brown crystalline solid (150 mg) thus obtained from the benzene eluate was not pure but contained appreciable amounts of $[RuCl_2(HL^5)(L^5)]$ (2g), as was evident from e.s.r. and electrochemical data. Repeated trials were made to obtain the complex in pure form but without success (Found: C, 44.9; H, 3.6; Cl, 12.7; N, 7.6. Calc. for $C_{18}H_{17}Cl_2N_2O_4Ru$: C, 43.5; H, 3.4; Cl, 14.3; N, 5.6%).

Reaction of $RuCl_3\cdot 3H_2O$ *with Biacetyl Oxime* (HL^4).—The reaction was carried out following the same procedure as above. The yield of the brown solid was very low (*ca.* 10%). The presence of small amounts of $[RuCl_2(HL^4)(L^4)]$ (2f), in this preparation was evidenced from the electrochemical data. The cathodic peak current (i_{pc}) of the prepared mixture was 2 μA in the region of the ruthenium(III)–ruthenium(II) couple (see below). Since under the same conditions pure $[RuX_2(HL)(L)]$ has i_{pc} *ca.* 40 μA, the present preparation has only 5% of (2f).

RESULTS AND DISCUSSION

Structural Considerations.—$RuCl_3\cdot 3H_2O$ reacts with HL in ethanol as shown in equation (11). Addition of

$$RuCl_3 + 2HL \longrightarrow [RuCl_2(HL)(L)] + HCl \qquad (11)$$

LiBr to the reaction mixture yields the bromo-analogue. The red-violet crystalline complexes are soluble in common organic solvents but are insoluble in water. The solutions are non-electrolytes. The complexes could be obtained in good yield and in pure form only for the ligands having R′ = Ph (HL^1—HL^3). The ligands having R′ = Me (HL^4, HL^5) give rise to intractible mixtures which however contain small amounts of $[RuX_2(HL)(L)]$ as evidenced from e.s.r. and electrochemical studies. Physical data of the complexes are in Table 1.

$[RuX_2(HL)(L)]$ has a magnetic moment corresponding to low-spin ruthenium(III) ($S = \frac{1}{2}$). Structure (2) is characterised[5] by single ν(RuX) vibration, relatively low ν(CO) and high ν(NO), and the absence of observable ν(OH) bands. Effectively, a planar tetradentate ligand is formed by the junction of two bidentate ligands *via* oxime–oximato O···H···O hydrogen bonding. A similar structural type occurs[6] in ruthenium complexes of arylazo-oxime $[RuX_2(HA)(A)]$ [HA = RC(=NOH)–N=N–aryl]. The low CO stretching frequencies in $[RuX_2(HL)(L)]$ are indicative of electron delocalisation.[2,5] It is reasonable to assume that the charge-separated canonical form ($>C^{+}{-}O^{-}$) of the carbonyl function binds ruthenium(III) better than the form $>C{=}O$. Such binding in turn augments the former canonical form. The much superior yield and stability of the complexes (2) with ligands having R′ = Ph compared to those with R′ = Me is readily rationalised in terms of resonance structures of type $Ph^{+}{=}\overset{|}{C}{-}O^{-}$ which have no counterpart when Ph is replaced by Me. The earlier interpretation[5] of the low ν(CO) value in $[RuX_2(HL)(L)]$ was an oversimplification.

TABLE 1

Selected physical data for $[RuX_2(HL)(L)]$ (2)

	Complex	I.r. data[a,b] ν(CO)/cm^{-1}	ν(RuX)/cm^{-1}	$\mu_{eff.}$/ B.M.[c]	Electronic spectral data[d,e] λ/nm (ε/dm^3 mol^{-1} cm^{-1})
(2a)	$[RuBr_2(HL^1)(L^1)]$	1 505	290	1.87	688 (sh), 572(8 800), 502(8 500), 330(22 800), 246(17 100)
(2b)	$[RuCl_2(HL^2)(L^2)]$	1 515	354	1.96	740(130), 545(8 000), 385(9 500)
(2c)	$[RuBr_2(HL^2)(L^2)]$	1 510	282	1.93	755(190), 540(8 900), 505(9 000)
(2d)	$[RuCl_2(HL^3)(L^3)]$[f]	1 530	358	1.80	772(330), 565(11 200), 450 (sh) (7 000), 380 (sh) (12 200)
(2e)	$[RuBr_2(HL^3)(L^3)]$[g]	1 530	299	2.20	790(390), 552(9 400), 510(9 500)

[a] 4 000—400 cm^{-1} in KBr disc, and 400—100 cm^{-1} in polyethylene disc. [b] ν(NO) appears in all complexes near 1 300 cm^{-1}. [c] $Hg[Co(SCN)_4]$ as standard. [d] In CH_2Cl_2 at 298 K. [e] (sh) = shoulder. [f] Electronic spectral data in CH_3CN: 760(320); 544(9 660); 370 (sh) (13 000). [g] Electronic spectral data in CH_3CN: 775(350); 522(7 000); 420 (sh) (7 500); 380(12 200).

Charge-transfer Spectra.—In the visible region two characteristic bands are observed, at *ca.* 750 and *ca.* 530 nm. The latter band often splits into a doublet in the bromo-species. Ruthenium(III) and ruthenium(II) complexes of unsaturated ligands usually display ligand ⟶ metal (l.m.)[21,22] and metal ⟶ ligand (m.l.)[23] charge-transfer (c.t.) spectra respectively. In $[RuX_2(HL)(L)]$ the bands in the visible region are assigned to a l.m.c.t. transition of type π(ligand) ⟶ t_{2g}(metal). Such transitions are known[6,21] to occur at relatively low energies. For a given HL, the l.m.c.t. band energy follows the order Cl > Br and for a given X, the order is $HL^2 > HL^3$. The correlation of these orders with electrochemical reduction potentials is discussed later. A possible effect of the l.m.c.t. band on the e.s.r. spectra of $[RuX_2(HL)(L)]$ is considered below.

Electron Spin Resonance Spectra.—All the complexes show strong and well defined e.s.r. spectra in the polycrystalline phase even at room temperature (Table 2). In one case, it has been demonstrated that the spectral nature does not change significantly in going to liquid nitrogen temperature or to dilute frozen glasses.[5] The same applies to the remaining complexes. The complex $[RuCl_2(HL^5)(L^5)]$ could not be isolated in the pure form but its presence in the impure preparation is clear in the e.s.r. spectrum. All spectra are axial in nature and the evaluated[24] $g_{\parallel}$ and $g_{\perp}$ values and results of computations are in Table 2.

TABLE 2

Assignment of experimental *g* tensors and e.s.r. parameters obtained for $[RuX_2(HL)(L)]$ (2)

Complex	$g_{\perp}$[*]	$g_{\parallel}$[*]	Solution no.	$g_{\perp}$	$g_{\parallel}$	A	B	k	Δ/λ	$\Delta E_1/\lambda$	$\Delta E_2/\lambda$
(2a)	2.613	1.880	(1)	−2.613	1.880	0.125	0.992	1.84	6.020	5.698	6.609
			(2)	−2.613	−1.880	0.768	0.640	1.29	0.242	1.438	1.590
(2b)	2.470	1.849	(1)	−2.470	1.849	0.153	0.988	1.21	4.943	4.663	5.553
			(2)	−2.470	−1.849	0.775	0.632	1.21	0.210	1.444	1.577
(2c)	2.558	1.861	(1)	−2.558	1.861	0.141	0.990	1.52	5.381	5.081	5.981
			(2)	−2.558	−1.861	0.770	0.638	1.26	0.232	1.439	1.586
(2d)	2.446	1.962	(1)	−2.446	1.962	0.065	0.998	2.47	10.880		
			(2)	−2.446	−1.962	0.785	0.620	1.22	0.164	1.453	1.559
(2e)	2.514	1.851	(1)	−2.514	1.851	0.149	0.989	1.34	5.072	4.786	6.043
			(2)	−2.514	−1.851	0.772	0.635	1.23	0.223	1.441	1.581
(2g)	2.525	1.867	(1)	−2.525	1.867	0.139	0.990	1.45	5.444	5.142	6.043
			(2)	−2.525	−1.867	0.773	0.635	1.24	0.220	1.442	1.581

[*] Experimentally observed *g* values.

Values of A, B, Δ, ΔE_i, and k were computed from equations (6)—(10). Two solutions, numbered (1) and (2), emerged in each case (Table 2). The two solutions differ in the sign of $g_{\parallel}$ and the magnitude of Δ. Since the value of λ is *ca.* 1 000 cm^{-1} (ref. 16), Δ in solution (2) is *ca.* 200 cm^{-1}. This is believed to be too small for the present structural situation. Significantly, in low-spin t_{2g}^6 species (Co^{III}) of type CoN_4Cl_2, Δ values are quite large.[25] The Δ values (*ca.* 5 000 cm^{-1}) of solution (1) are much more reasonable even though this solution leads to higher values of k. We accept solution (1) in preference to solution (2). In solution (1), B is much larger than A. Simply stated, the ground Kramers doublet is a nearly pure d_{xy} orbital. Since the hole is located in this orbital, the sign of Δ is positive.[15]

The strict symmetry of the complexes ($RuX_2N_2O_2$ co-ordination sphere) cannot be higher than C_{2v}. The observed axial e.s.r. symmetry is indicative of the presence of an *effective* C_3 or C_4 axis. In a simple description, the molecule may have an effective four-fold axis of symmetry (z direction) coincident with the RuX_2 axis, while the base (xy plane) has an averaged N_2O_2 co-ordination. Considering the position of X, N, and O in the spectrochemical series, one may anticipate the d-orbital energy order $d_{xz}, d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$. The observed e.s.r. ground state (hole in d_{xy}) is in accord with this. Hill[15f] has shown that in $[Ru(PEt_2Ph)_3Cl_3]$, the d_{xy} level is of lower energy than $d_{xz,yz}$ (Δ negative) and this is attributed to a strong repulsive π interaction between $d_{xz,yz}$ and filled π orbitals on Cl. Sakaki *et al.*[15g] have shown that a similar situation exists in $[Ru(NH_3)_5X]^+$. In our complexes the unsaturated ligand (on xy plane) has empty π orbitals which could preferentially stabilise $d_{xz,yz}$.

Much of the reported e.s.r. data on ruthenium(III) are on complexes of S, P, and As donors.[16-18] No results are available on any system which is closely analogous to the complexes (2). However, a comparison can still be made with other systems.[18-20] Two solutions are often obtained but one of these is accepted on the basis of chemical and other arguments.[18,19] Interestingly, *in all cases* the accepted solution has $g_\perp$ (or g_x and g_y) negative and $g_\parallel$ (or g_z) positive, as in the case of complexes (2). This appears to be a general result.

A comment on the values of k is in order. In calculations of the present type, it is hardly meaningful to equate k with covalency. It acts as a ' sink ' for various unaccounted effects[19] and in this manner values of k >1 arise.[18] In the present complexes, barring one case, the k values of solutions of HL lie in the range 1.20—1.85. The inter-relationships of k, Δ, and g_i were examined with the help of equations (6)—(10) and relevant plots and data are recorded elsewhere.[26] Of particular interest here is the variation of k with $g_\parallel$. The region useful for the present work is displayed in Figure 1. The signs of g_i are ignored in the following discussion. At a given value of $g_\parallel$, the lower the magnitude of $g_\perp$, the smaller is the value of k. At a given $g_\perp$, k increases first slowly and then rapidly as $g_\parallel$ increases. In our systems, $g_\perp$ lies in the range 2.4—2.6 and it can be seen that in this range k increases very rapidly beyond $g_\parallel =$ 1.85. Thus the larger values of k observed by us are intimately connected with $g_\parallel$ being close to 2.0.

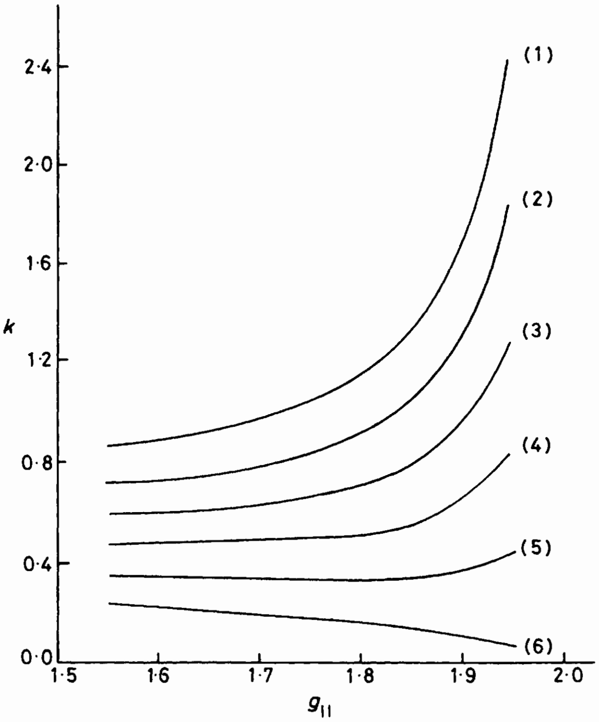

FIGURE 1 Variation of k with $g_\parallel$: $g_\perp$ = 2.50 (1), 2.40 (2), 2.30 (3), 2.20 (4), 2.10 (5), and 2.00 (6)

One reason for high $g_\parallel$ may be the contribution of the low-energy l.m.c.t. states (see above) to the ground wavefunctions.[18] The g value of the l.m.c.t. state ($\pi^1 t_{2g}^6$) is expected to be close to that of the free electron. The l.m.c.t. transition may be so polarised that it influences $g_\perp$ relatively slightly. While the problem is under further scrutiny, we add that in $[RuX_2(HA)(A)]$ the l.m.c.t. bands are at even lower energies (*ca.* 580 and *ca.* 1 000 nm) and observed $g_\parallel$ values come even closer[6] to 2.0.

Electrochemical Reduction.—All complexes display cyclic redox activity on both positive and negative sides of s.c.e. (Table 3). Cylic voltammetric (c.v.) response on the positive side occurs near 0.4 V and is characterised by a peak-to-peak separation (ΔE_p) of 70 mV at scan rates (v) $\leqslant$50 mV s^{-1} in acetonitrile. The presence of a nearly reversible one-electron process (12) is indicated. One-electron involvement is confirmed by constant potential coulometry.

$$\underset{(2)}{[Ru^{III}X_2(HL)(L)]} + e^- \rightleftharpoons \underset{(3)}{[Ru^{II}X_2(HL)(L)]^-} \quad (12)$$

Since the couple is nearly reversible, the gross structures of (2) and (3) are believed to be alike. The oxidising power of $[RuX_2(HL)(L)]$ is much greater than that of *trans*-$[RuCl_2(NH_3)_4]^+$ ($E_{298}^0 = -0.43$ V),[27] and is comparable to that of *trans*-$[RuCl_2(HA)(A)]$ (E_{298}^0 *ca.* 0.5 V),[6] and is much less than that of *trans*-$[RuCl_2B_2]$ ($E_{298}^0 = 0.93$ V) (B = 2-phenylazopyridine).[28] The process (12) is less reversible (ΔE_p *ca.* 130 mV at v = 50 mV s^{-1}) in dichloromethane. The E_{298}^0 values are also shifted to lower potentials in this solvent. These effects can arise from the lower dielectric constant of dichloromethane.[29] On increasing v, ΔE_p increases, and the heterogeneous rate constant [14] ($k_{s,h}$) of the electron-transfer reaction was determined in several cases. The diffusion coefficients (D) were determined chronoamperometrically.[12,13]

The process (12) was also studied using phase-sensitive alternating current cyclic voltammetry (p.s.a.c.c.v.) in acetonitrile with peak-to-peak amplitude (ΔE) of 10 mV at frequencies (ω) 22 and 35 Hz, and v = 0.5—10 mV s^{-1} (Table 3 and Figure 2). At very slow scan rates the peak potentials for forward (E_{pf}) and backward (E_{pb}) scans coincide.

TABLE 3

Electrochemical data [a] at 298 K

		c.v. Data, ruthenium(III)–ruthenium(II) couple						p.s.a.c.c.v. Data,[b] ruthenium(III)–ruthenium(II) couple		
		Formal potential			Rate data [c]		Ligand reduction [d]			
Complex	Solvent	v/mV s^{-1}	$E_{298}°$/V	ΔE_p/mV	10^5D/cm^2 s^{-1}	$10^2k_{s,h}$/cm s^{-1}	$-E_{pc}$/V	v/mV s^{-1}	$E_{298}°$/V	δ/mV
(2a) [e]	CH_3CN	50	0.53	100	0.68	0.45	f	f	f	f
(2b) [g]	CH_3CN	50	0.30	70	1.57	0.98	1.20	0.5—10	0.30	105
	CH_2Cl_2	20	0.27	150	0.94	0.11	f			
(2c) [h]	CH_3CN	50	0.37	70	1.16	1.35	1.19	0.5—10	0.36	105
	CH_2Cl_2	20	0.30	137	1.25	0.15	f			
(2d)	CH_3CN	50	0.46	70	1.28	1.50	1.15	0.5—10	0.47	100
	CH_2Cl_2	20	0.37	130	1.19	0.17	f			
(2e)	CH_3CN	50	0.50	70	1.20	1.75	1.12	0.5—10	0.51	100
	CH_2Cl_2	20	0.40	110	0.91	0.20	f			
(2f) [i]	CH_3CN	50	0.26	65	f	f	f	1	0.26	100
(2g) [i]	CH_3CN	50	0.40	65	f	f	f	1	0.40	100

[a] Supporting electrolyte $[NEt_4][ClO_4]$ (0.1 mol dm^{-3}); all potentials are referred to s.c.e.; $E_{298}° = 0.5(E_{pa} + E_{pc})$. [b] ω = 35 Hz; ΔE = 10 mV (peak-to-peak). [c] $k_{s,h}$ was determined in the range of v = 20—200 mV s^{-1}. [d] In ligand reduction, only cathodic peak was observed. [e] Pure (2a) gave only a small response in CH_3CN solution. On addition of $HClO_4$ the response is augmented, and finally reached the full height in 10^{-3} mol dm^{-3} $HClO_4$ in CH_3CN. The complex appears to become partially deprotonated in CH_3CN solvent. [f] Not measured. [g] Coulometric data: 10.01 mg (2b) electrolysed at 0.0 V: $Q_{calc.} = 1.94$; $Q_{found} = 1.85$. [h] Coulometric data: 5.50 mg (2c) reduced at 0.0 V: $Q_{calc.} = 0.90$; $Q_{found} = 0.87$. [i] Impure sample.

$$E_{298}{}^{0} = E_{pf} = E_{pb} \qquad (13)$$

The $E_{298}{}^0$ values thus obtained are within ±10 mV of the c.v. values. The width (δ) at half-peak height is *ca.* 100 mV, showing that the process (12) is nearly 'a.c. Nernstian'.[30] The peak height is proportional to $\omega^{\frac{1}{2}}$. On increasing the scan rate, E_{pf} and E_{pb} diverge showing that the direct current (d.c.) process is not ideally Nernstian; a result which is in agreement with the observed c.v. behaviour. At $v > 20$ mV s^{-1}, the voltammogram progressively diminishes in height with broadening and

$$\omega \Delta E \gg v \qquad (14)$$

distortion due to breakdown of the relation (14).[30,31] However, the cross-over potential (E_{co}) of the forward and backward scans remains virtually invariant. If the charge-transfer coefficient (α) is 0.5, we have equation (15). This relation is found to be applicable to our system.

$$E_{co} = E_{298}{}^{0} \qquad (15)$$

For a given HL, $E_{298}{}^0$ follows the order Br > Cl. Since in the reduction an electron is added to the t_{2g} level of ruthenium, the results imply the energy order t_{2g}(Br) < t_{2g}(Cl). If it is assumed that the ligand π orbitals have approximately the same energy in both complexes, the red shift of the l.m.c.t. band and the positive shift of $E_{298}{}^0$ in going from Cl to Br are in consonance. For a given X, the $E_{298}{}^0$ value changes on variation of HL ligands. It becomes less positive as the R (and R') groups are made more electron-donating. The observed order is thus $HL^1 > HL^3 > HL^5 > HL^2 > HL^4$.

In addition to the reversible couple (12) near 0.4 V, an irreversible process is observed at *ca.* −1.1 V in all the complexes. No appreciable current on the anodic side could be observed even at high scan rates (v = 500 mV s^{-1}). The current height is similar to that of cathodic peak current at *ca.* 0.4 V at the same v value. This shows

$$\underset{(3)}{[RuX_2(HL)(L)]^-} + e^- \longrightarrow \underset{(4)}{[RuX_2(HL)(L)]^{2-}} \qquad (16)$$

that the reduction involves one electron. The lack of anodic response may be due to the fact that (4) is unstable and undergoes fast chemical destruction. The nature of (4) is not clear at the present time and it is not known whether in couple (16) the electron is added to the metal or to the ligand. However, ruthenium complexes of unsaturated ligands are known [28,32] to display c.v. responses at potentials below −1.0 V due to ligand reduction. It is likely that the process (16) is also localised on the ligand.

Reaction of $[RuX_2(HL)(L)]$ *with Reducing Agents.*—Coulometrically reduced solutions containing (3) are deep blue. Usually, $[RuCl_2(HL)(L)]^-$ is more stable than $[RuBr_2(HL)(L)]^-$. The complex (2) is also reduced instantly by hydroquinone (H_2quin) in acetonitrile to give the same blue solution. Excess H_2quin is needed for complete reduction and the reaction is reversed by the addition of acid. The presence of equilibrium (17) is indicated. Other reducing agents, *e.g.* hydrazine, ethanol, iron(II) ion, *etc.*, are also effective in bringing about the conversion (2) ⟶ (3).

$$\underset{(2)}{2\,[\mathrm{RuX_2(HL)(L)}]} + \mathrm{H_2quin} \rightleftharpoons \underset{(3)}{2\,[\mathrm{RuX_2(HL)(L)}]^-} + 2\,\mathrm{H^+} + \mathrm{quin} \quad (17)$$

The deep blue solutions exhibit an m.l.c.t. band in the visible region. Representative data are [λ/nm (ε/dm^3 mol^{-1} cm^{-1})]: (2b), 648 (13 900); (2c) 635(20 300); (2d), 648(16 350); (2e), 635(16 150). For a particular HL, the m.l.c.t. band energy shifts as Br > Cl. The order is opposite to that observed for the l.m.c.t. band in (2), as expected. Usually, the reduced species are just stable for spectral measurements to be carried out immediately after reduction. However, in the case of (2a), the coulometrically reduced solution becomes rapidly oxidised in air into the parent complex. The possibility of using this complex as a redox catalyst is under study.

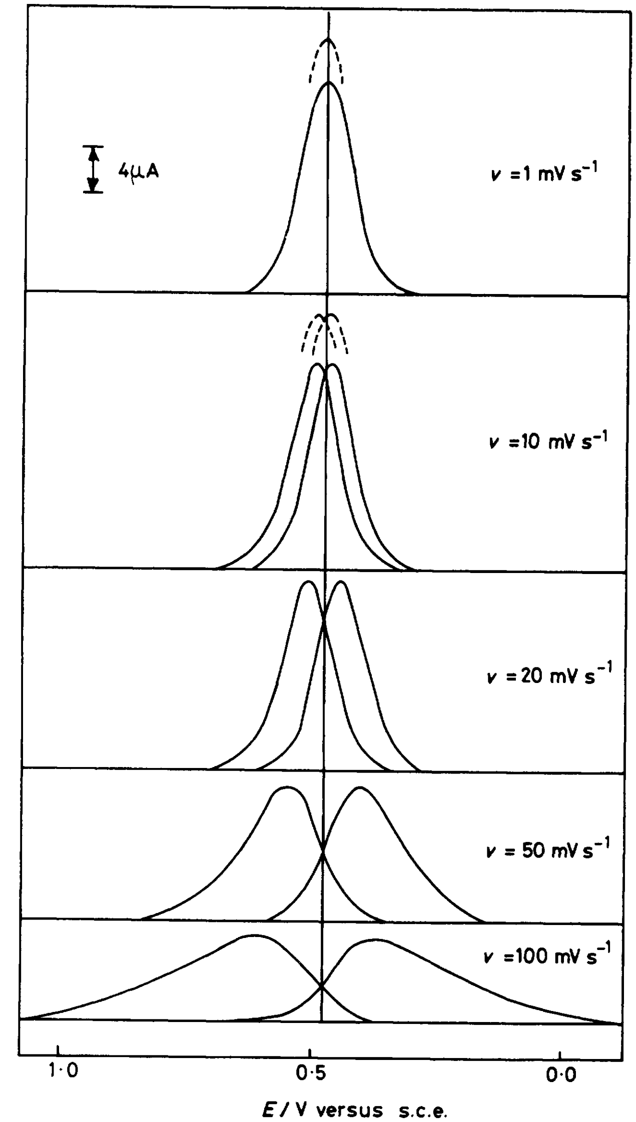

FIGURE 2 Phase-sensitive cyclic voltammograms of [RuCl$_2$-(HL^3)(L^3)] (1.0 × 10^{-3} mol dm^{-3}) in CH$_3$CN: (——) at 22 Hz, (— — —) at 35 Hz

Reaction of [RuX$_2$(HL)(L)] *with Base.*—The electrochemical response at *ca.* 0.4 V is dramatically affected by addition of NEt$_3$ (Figure 3). It decreases progressively and linearly with the amount of base added. At a complex : base mol ratio of 1 : 1, the original cathodic and anodic responses vanish. The voltammogram reappears on addition of HClO$_4$. The full current heights are re-established when NEt$_3$: HClO$_4$ becomes 1 : 1. The process involved is thus (18). The deprotonated species, [RuX$_2$(L)$_2$]$^-$, is electroinactive at *ca.* 0.4 V.

$$[\mathrm{RuX_2(HL)(L)}] \underset{\mathrm{HClO_4}}{\overset{\mathrm{NEt_3}}{\rightleftharpoons}} [\mathrm{RuX_2(L)_2}]^- \quad (18)$$

In the deprotonation–protonation process (18), it will be reasonable to implicate the transfer of the bridging oxime proton. There is a symbiotic relationship between electron transfer and proton transfer. Addition of a proton facilitates the addition of an electron. The inter-relationship of electron transfer and proton transfer in co-ordination chemistry and biology is becoming increasingly clear in recent times.[33,34] The interesting point is that the electron transfer involves the metal ion while the proton transfer is located on the ligand. In effect, we have a remote interaction dramatically controlling the electron transfer.

Concluding Remarks.—We can now summarise some of the conclusions drawn and link up the several kinds of studies reported above. We have demonstrated that isonitrosoketones bind the *trans*-dihalogenoruthenium(III) moiety quite effectively. An important feature of the ligands (1) is the intramolecular hydrogen bonding. This feature, though uncommon, is now known to occur in the arylazo-oximates [RuX$_2$(HA)(A)].[6] The removal and re-insertion of the bridge proton in (2) is probed using the variation in electrochemical redox response. Metal-assisted delocalisation of ligand electrons in (2) is apparent in the i.r. spectra and such delocalisation appears to play an important role in determining the relative stability among complexes differing only in substituents. The presence of a low-lying ligand ⟶ metal delocalised state is seen in electronic spectra. This state appears to make considerable contribution to the ground function thus affecting e.s.r. *g* values and other parameters. The observation of a low-lying spectrochemical l.m.c.t. state (internal redox) can be viewed together with the fact that the metal centre in [RuX$_2$(HL)(L)] acts as a good oxidising agent, undergoing one-electron reduction both electrochemically and chemically. The spectral, electrochemical, and electronic effects are well correlated. Thus, the shift of the formal potential shows parallelism with the position of the halogens in the

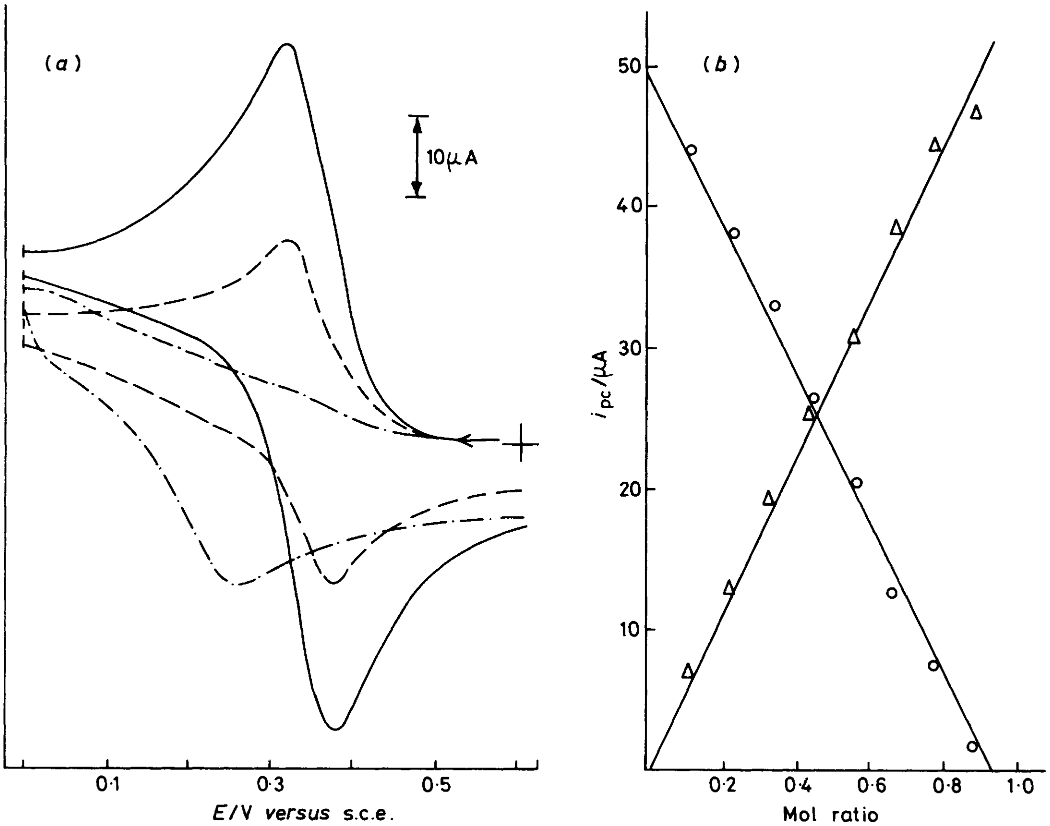

FIGURE 3 Effect of deprotonation on voltammetric response of $[RuCl_2(HL^2)(L^2)]$ in CH_3CN. (a) Cyclics at different (NEt_3) : complex mol ratios: (———) 0.0, (— — —) 0.49, (— · — · —) 0.83. (b) Linear plot of i_{pc} *versus* NEt_3 : complex mol ratios during deprotonation (○) and $HClO_4$: NEt_3 mol ratios during reprotonation (△)

spectrochemical series, with l.m.c.t. band energies as well as with the electron-donating character of HL.

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REFERENCES

[1] A. Chakravorty, *Coord. Chem. Rev.*, 1974, **13**, 1.

[2] C. Bremard, G. Nowogrocki, and S. Sueur, *J. Chem. Soc., Dalton Trans.*, 1977, 2307.

[3] M. V. Savostina, O. A. Shpigun, and N. V. Klimova, *Chem. Abs.*, 1979, **90**, 161468g.

[4] A. R. Chakravarty and A. Chakravorty, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 307.

[5] A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 275.

[6] A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 3138.

[7] C. L. Raston, A. H. White, and R. M. Golding, *J. Chem. Soc., Dalton Trans.*, 1977, 329.

[8] C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1976, 1915.

[9] W. L. Semon and V. R. Damercell, 'Organic Synthesis Collective,' ed. A. H. Blatt, John Wiley and Sons, Inc., London, 1943, vol. 2, p. 204.

[10] W. H. Hartung and F. Crossby, 'Organic Synthesis Collective,' ed. A. H. Blatt, John Wiley and Sons, Inc., London, 1943, vol. 2, p. 363.

[11] A. I. Vogel, 'Practical Organic Chemistry,' 3rd edn., ELBS Longman Group Ltd., London, 1965, p. 720.

[12] P. J. Lingane, *Anal. Chem.*, 1964, **36**, 1723.

[13] P. Delahay, 'New Instrumental Methods in Electrochemistry,' Interscience, New York, 1954, ch. 3.

[14] R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351; R. S. Nicholson and I. Shain, *ibid.*, 1964, **36**, 706.

[15] (*a*) K. W. H. Stevens, *Proc. R. Soc., Ser. A*, 1953, **219**, 542; (*b*) B. Bleany and M. C. M. O'Brien, *Proc. Phys. Soc. London, Sect. B.*, 1956, **69**, 1216; (*c*) J. S. Griffith, 'The Theory of Transition Metal Ions,' Cambridge University Press, London, 1961, p. 364; (*d*) J. S. Griffith, *Nature*, 1957, **180**, 30; (*e*) B. F. Figgis, *Trans. Faraday Soc.*, 1961, **57**, 198; (*f*) N. J. Hill, *J. Chem. Soc. Faraday Trans. 2*, 1972, 427; (*g*) S. Sakaki, N. Hagiwara, Y. Yanase, and A. Ohyoshi, *J. Phys. Chem.*, 1978, **82**, 1917.

[16] A. Hudson and M. J. Kennedy, *J. Chem. Soc., A*, **1969**, 1116.

[17] L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J. Chem. Soc., Dalton Trans.*, 1973, 1770; P. T. Manoharan, P. K. Mehrotra, M. M. Taquikhan, and R. K. Andal, *Inorg. Chem.*, 1973, **12**, 2753; O. K. Medhi and U. Agarwala, *J. Inorg. Nucl. Chem.*, 1980, **42**, 1413; S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 1971, 803; R. E. DeSimone, T. Ontko, L. Wardman, and E. L. Blinn, *Inorg. Chem.*, 1975, **14**, 1313.

[18] O. K. Medhi and U. Agarwala, *Inorg. Chem.*, 1980, **19**, 1381.

[19] R. E. DeSimone, *J. Am. Chem. Soc.*, 1973, **95**, 6238.

[20] R. E. DeSimone and R. S. Drago, *J. Am. Chem. Soc.*, 1970, **92**, 2343; J. A. Stanko, H. J. Peresie, R. A. Bernheim, R. Wang, and P. S. Wang, *Inorg. Chem.*, 1973, **12**, 634; W. Reiff and R. E. DeSimone, *Inorg. Chem.*, 1973, **12**, 1793.

[21] G. M. Bryant and J. E. Fergusson, *Aust. J. Chem.*, 1971, **24**, 275; K. S. Murray, A. M. vanden Bergen, and B. O. West, *Aust. J. Chem.*, 1978, **31**, 203; B. P. Sullivan, D. J. Salmon, and T. J. Meyer, *Inorg. Chem.*, 1978, **17**, 3334.

[22] C. K. Jorgensen, 'Absorption Spectra and Chemical Bonding in Complexes,' Pergamon Press, Oxford, 1962; H. Hartmann and C. Buschbeck, *Z. Physik. Chem.*, 1957, **11**, 120.

[23] F. Felix, J. E. Fergusson, H. U. Güdel, and A. Ludi, *J. Am. Chem. Soc.*, 1980, **102**, 4096; G. M. Bryant, J. E. Fergusson, and H. K. J. Powell, *Aust. J. Chem.*, 1971, **24**, 257; R. J. Watts, J. S. Harrington, and J. V. Houten, *Inorg. Organomet. Photochem.*, 1978, **168**, 57.

[24] F. K. Kneubühl, *J. Chem. Phys.*, 1969, **33**, 1074.

[25] R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709.

[26] A. R. Chakravarty, Ph.D. Thesis, Calcutta University, Calcutta, 1981.

[27] H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460.

[28] S. Goswami, A. R. Chakravarty, and A. Chakravorty, *Inorg. Chem.*, 1981, **20**, 2246.

[29] C. V. Senoff, *Coord. Chem. Rev.*, 1980, **32**, 11.

[30] W. L. Underkolfer and I. Shain, *Anal. Chem.*, 1965, **37**, 218; A. M. Bond, R. J. O'Halloran, I. Ruzic, and D. E. Smith, *ibid.*, 1976, **48**, 872.

[31] R. S. Nicholson and I. Shain, *Anal. Chem.*, 1965, **37**, 178.

[32] J. L. Sadler and A. J. Bard, *J. Am. Chem. Soc.*, 1968, **90**, 1979; J. C. Darbrowiak, D. F. Fisher, F. C. McElroy, and D. J. Macero, *Inorg. Chem.*, 1979, **18**, 230; B. P. Sullivan, D. J. Salmon, T. J. Meyer, and J. Peedin, *Inorg. Chem.*, 1979, **18**, 3369; P. Bandyopadhyay, R. N. Mukherjee, P. Ghosh, and A. Chakravorty, unpublished work.

[33] J. G. Mohanty and A. Chakravorty, *Inorg. Chem.*, 1976, **15**, 2912; 1977, **16**, 1561; D. Datta, P. K. Mascharak, and A. Chakravorty, *ibid.*, 1981, **20**, 1673.

[34] H. Beinert, *Coord. Chem. Rev.*, 1980, **33**, 55; R. J. P. Williams, *Chem. Soc. Rev.*, 1980, **9**, 281; P. Michell, *Chem. Br.*, 1981, **17**, 14.