Ketoximato-complexes. Part 3.‡ Structure and Properties of Tris Chelates of Cobalt(III), Iron(II), and Ruthenium(II)

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A number of tris chelates derived from dihydrogenviolurate (H_2va^-) and 1,3-dimethylviolurate ($dmva^-$) have been synthesized. Complexes of general formula $[ML_3]^{n-}$ ($M = Co^{III}$, $n = 0$; $M = Fe^{II}$ or Ru^{II}, $n = 1$; $L = H_2va$ or dmva) are described and characterized by i.r., u.v.–visible, and ^1H n.m.r. spectra. Infrared data support the assumption of the same *fac* co-ordination structure for all the complexes in the solid state. The ^1H n.m.r. spectra are in accordance with an octahedral arrangement in the *fac* configuration in solution. The ^1H n.m.r. shifts are a probe of electron-density changes at the N(1) and N(3) sites of the co-ordinated heterocycle. Measurements of pK_a for the $[M(H_2va)_3]^{n-}$ complexes are presented and are consistent with the n.m.r. data. The energies of the $\pi \rightarrow \pi^*$ and $d \rightarrow \pi^*$ electronic transitions of the protonated and deprotonated species provide information about the energies of the molecular orbitals of the violurate ligand. The results are interpreted in terms of Lewis-acid charge withdrawal and π-back bonding.

NITROSOARENES and their derivatives are interesting ligands since the compounds have low-lying π^* systems which may be accessible for back bonding.[1-5] Earlier [6] we reported the preparation and stereochemistry of a new series of ruthenium–mononitrosyl complexes *cis*-$[RuL_2(NO)X]$, where L represents the unsymmetrical bidentate ligands H_2va^- (dihydrogenviolurate, the monoanion of 1*H*,3*H*,5*H*-pyrimidine-2,4,5,6-tetraone 5-oxime) or $dmva^-$ (1,3-dimethylviolurate, the monoanion of 1,3-dimethylpyrimidine-2,4,5,6-tetraone 5-oxime) and $X = Br$ or Cl. All these complexes possess nitrosyl groups with high ν(NO) stretching frequencies.[7] The unusual reactivity of the nitrosyl ligand[8] has been attributed to a considerable degree of NO^+ character in the formal d^6 Ru^{II}–NO^+ linkage caused by the relatively high formal oxidation state of the metal and the competitive back bonding with the L ligands.

Several means for obtaining quantitative information concerning the nature of metal-to-ligand π bonding have been previously described.[9] More recently, n.m.r. studies demonstrate that chemical-shift changes are a promising means of directly observing π-back bonding effects.[10,11] The mutual effects of the nitrosyl and violurate ligands in the $[RuL_2(NO)X]$ complexes have been studied previously.[12] In the present work we describe experimental evidence concerning the effect of metal ions on the heterocyclic ligands in d^6 complexes of similar structure: $[Co^{III}L_3]$, $[Fe^{II}L_3]^-$, and $[Ru^{II}L_3]^-$, which include metal centres that have been shown to be non-π-back bonding, as well as those which are known to participate in π-back bonding.

EXPERIMENTAL

Reagents.—AnalaR grade $Co[NO_3]_2 \cdot 6H_2O$, $Na_3[Co(NO_2)_6]$, $Fe[SO_4] \cdot 9H_2O$, barbituric (1*H*,3*H*,5*H*-pyrimidine-2,4,6-trione), 1,3-dimethylbarbituric, and violuric acids were used without further purification. The salt $Na_2[Ru(NO)(NO_2)_4(OH)] \cdot 2H_2O$ was obtained as described previously.[6] 1,3-Dimethylvioluric acid and the salts $Na[H_2va]$ and Na[dmva] were obtained in our laboratory by well known procedures. Elemental analyses (C, H, N, K, Ba) were undertaken by the Microanalytical Laboratory of C.N.R.S., Villeurbanne, France. Ruthenium analysis was performed by a method described previously.[6]

Preparation of the Ketoximato-complexes.—$[Co^{III}(H_2va)_3]$. This compound was prepared using either the procedure described in ref. 13 or $Na_3[Co(NO_2)_6]$ and barbituric acid as starting materials. The compound $Na_3[Co(NO_2)_6]$ (4.3 g, 10.7 mmol) was dissolved in water (150 cm^3) and barbituric acid (4.1 g, 32 mmol) was introduced into the solution. The solution was maintained at 50 °C during 24 h. After cooling at room temperature and filtration to remove a small amount of violuric acid, the solution was allowed to crystallize over a few days. The resulting orange-red crystals were filtered off and washed several times with cold water and ethanol. The $[Co(H_2va)_3] \cdot 5H_2O$ crystals were then dried at 150 °C, yield 80% (Found: C, 27.1; H, 1.5; N, 24.0. Calc. for $C_{12}H_6CoN_9O_{12}$: C, 27.3; H, 1.15; N, 23.9%).

$[Co^{III}(dmva)_3]$. The procedure was the same as for $[Co(H_2va)_3]$ except that 1,3-dimethylbarbituric acid was used instead of barbituric acid. The complex $[Co(dmva)_3]$ precipitated immediately as an orange-red powder and was dried at 150 °C. Yield 90% (Found: C, 35.1; H, 3.6; N, 21.0. Calc. for $C_{18}H_{18}CoN_9O_{12}$: C, 35.35; H, 2.95; N, 20.6%).

$Na[Fe(H_2va)_3]$. The procedure was the same as that reported previously[14] (Found: C, 26.15; H, 1.95; N, 23.3. Calc. for $C_{12}H_6FeN_9NaO_{12}$: C, 26.35; H, 1.10; N, 23.1%).

$Na[Fe(dmva)_3]$. The procedure was analogous to that for $Na[Fe(H_2va)_3]$ (Found: C, 34.0; H, 3.3; N, 19.8. Calc. for $C_{18}H_{18}FeN_9NaO_{12}$: C, 34.3; H, 2.85; N, 20.0%).

The compounds $Na[Ru(H_2va)_3]$ and $Na[Ru(dmva)_3]$ were obtained as described in ref. 6. They gave satisfactory elemental analyses.

$K_4[Ru(Hva)_3]$. The compound $K[Ru(H_2va)_3]$ (0.2 g, 0.33 mmol) was added to water (2 cm^3). Addition of K[OH] (1 cm^3, 1 mol dm^{-3}) gave a deep violet solution. A dark compound was precipitated from this solution by slow addition of methanol. The resulting precipitate was collected, washed several times with methanol, and then dried.

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‡ For Parts 1 and 2 see refs. 16 and 26.

Yield 85% (Found: C, 20.1; K, 21.8; N, 17.6; Ru, 13.6. Calc. for $C_{12}H_3K_4N_9O_{12}Ru$: C, 19.95; K, 21.6; N, 17.45; Ru, 14.0%).

$Ba_{2.5}[Ru(Hva)_2(va)]$. The compound $Na[Ru(H_2va)_3]$ (0.2 g) was dissolved in degassed water (100 cm^3) under an argon atmosphere to which Na[OH] (30 cm^3, 10 mol dm^{-3}) was then added rapidly. The red solution became violet. A dark blue compound was precipitated by the slow addition of a saturated solution of $BaCl_2$. The resulting precipitate was collected, washed with ethanol and water, and dried at 120 °C under argon. Yield 95% (Found: C, 15.3; Ba, 37.3; N, 13.4; Ru, 10.6. Calc. for $C_{12}H_2Ba_{2.5}N_9O_{12}Ru$: C, 15.4; Ba, 36.65; N, 13.5; Ru, 10.8%).

Physical Measurements.—Ultraviolet–visible spectra were run on a Jobin and Yvon DUOSPAC 203 instrument, using jacketted quartz cells. Infrared spectra were obtained on a Perkin-Elmer 457 spectrometer using KBr plates. The potentiometric data were obtained on a radiometer PM 52 instrument using a glass electrode|solution|KCl (saturated solution)|calomel electrode system. The ^1H n.m.r. spectra were recorded on a Brücker WP 60 or on a Perkin-Elmer R 24B spectrometer at 37 ± 1 °C unless otherwise indicated. The solvent was $S(CD_3)_2O$ unless otherwise indicated.

The titrations of $[Co(H_2va)_3]$, $Na[Fe(H_2va)_3]$, and $Na[Ru(H_2va)_3]$ with Na[OH] were studied by spectrophotometry. The concentrations of the complexes were fixed by using known volumes of the respective stock solutions. For the iron complex titration, an excess of free ligand was added to prevent aquation; the concentration of H_2va^- was more than 100 times that of the iron complex. Corrections for the absorption of the free ligand were determined at the corresponding pH before calculation. The ionic strength was maintained at 0.5 mol dm^{-3} with sodium chloride. Circulation from the thermostatted flask (25 ± 0.1 °C) to the spectrophotometer cell was by micropump.

TABLE 1

Characteristic i.r. bands (cm^{-1}) of the ketoximato-complexes

$Na[H_2va]$	$Na[Ru(H_2va)_3]$	$K[Fe(H_2va)_3]$	$[Co(H_2va)_3]$	Tentative assignments
1 743vs	1 735vs	1 760vs	1 740vs	ν[C(2)=O]
1 710vs				
1 683vs	1 681vs	1 675vs	1 695vs	ν[C(1)=O]
1 572vs	1 595vs	1 600vs	1 595vs	ν[C(5)=N(5)] + ν(C=C)
	1 505s	1 510s	1 510s	ν[C(6)=O]
1 145m	1 210m	1 215m	1 235m	ν[N(5)–O(5)]
Na[dmva]	$Na[Ru(dmva)_3]$	$K[Fe(dmva)_3]$	$[Co(dmva)_3]$	
1 727vs	1 717vs	1 705vs	1 740vs	ν[C(2)=O]
1 710vs	1 665vs	1 645vs	1 700vs	ν[C(4)=O]
1 665vs				
1 520vs	1 561vs	1 555vs	1 570vs	ν[C(5)=N(5)] + ν(C=C)
	1 514vs	1 510vs	1 540vs	ν[C(6)=O]
1 235s	1 260s	1 260s	1 270s	ν[N(5)–O(5)]

Calculations.—The deprotonation constants K_{aj} and the molar absorption coefficients ε_{j+1} of absorbing species were obtained simultaneously from the spectrophotometric data by using a least-squares refinement program that minimizes the function $\sum_{1}^{N}(\bar{\varepsilon}_{obs.} - \bar{\varepsilon}_{calc.})^2$ [see Supplementary Publication No. SUP 23077 (12 pp.)[*]]. The average molar absorptivity coefficient $\bar{\varepsilon} = A/C_T l$ in which A is the absorbance, C_T the concentration of Co^{III}, Fe^{II}, or Ru^{II}, and l the spectrophotometer cell length (in cm). The procedure also computed the standard deviation. The final repartition of the residuals $|\bar{\varepsilon}_{obs.} - \bar{\varepsilon}_{calc.}|$ indicated that systematic errors were absent.

RESULTS

The preparations of $M[Fe(H_2va)_3]$ and $M[Fe(dmva)_3]$ were similar to those used previously to obtain suitable crystals of $[NH_4][Fe(H_2va)_3]\cdot4.5H_2O$:[14] by mixing iron(II) sulphate with an excess of ligand, $M[H_2va]$, or M[dmva] respectively with M = Na^+, K^+, or $0.5Ba^{2+}$. The ruthenium complexes $M[Ru(H_2va)_3]$ and $M[Ru(dmva)_3]$ were prepared as previously described,[6] the reagents being $[Ru(NO)(NO_2)_4(OH)]^{2-}$ and barbituric or 1,3-dimethylbarbituric acid. A detailed mechanism of the reaction has recently been reported.[15] The cobalt complexes $[Co(H_2va)_3]$ and $[Co(dmva)_3]$ were prepared using either cobalt(II) nitrate and the appropriate ligand or $Na_3[Co(NO_2)_6]$ and barbituric or 1,3-dimethylbarbituric acid. The products obtained by both methods were identical, as shown by the microanalyses and the ^1H n.m.r., i.r., and u.v.–visible spectra; however, the latter preparation appears to be easier. The ketoxime complexes and their *N*-methyl derivatives have been fully characterized by elemental analysis, and i.r. (Table 1), ^1H n.m.r. (Table 2), and u.v.–visible spectroscopy (Table 3).

A comparison between the positions and the relative intensities of the carbonyl and nitroso-i.r. absorptions of the ruthenium complexes enabled us[6] to assign the facial structure to the tris chelates $Na[Ru(H_2va)_3]$ and $Na[Ru(dmva)_3]$ in the solid state, the chelation occurring *via* the N(5) and O(6) atoms. Although the i.r. spectra of the iron and cobalt complexes are different from those of the ruthenium complexes, they present sufficient analogous features, Table 1, to allow the assumption of the same coordination for all the $[M(H_2va)_3]^{n-}$ and $[M(dmva)_3]^{n-}$ (n = 0 or 1; M = Co^{III}, Fe^{II}, or Ru^{II}). It is noteworthy that in the 650—4 000 cm^{-1} region the spectra of the complexes display no more bands than those of the corresponding free ligands; the assignments are the same as those reported in ref. 6. This is in agreement with the complete equivalence of the three chelates demonstrated by *X*-ray diffraction

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[*] For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1980, Index issue.

TABLE 2

Hydrogen-1 n.m.r. chemical shifts [a] of dihydrogenviolurato-complexes and their dimethyl derivatives

		Chemical shifts	
Compound	Solvent	N(1)	N(3)
$dmva^-$	$S(CD_3)_2O$	3.28 (3 H)	3.06 (3 H)
$[Co(dmva)_3]$	$S(CD_3)_2O$	3.40 (9 H)	3.11 (9 H)
$[Co(dmva)_3]$	PhCN [b]	2.85 (9 H)	2.6 (9 H)
$[Co(dmva)_3]$	CD_3CN	2.97 (9 H)	2.73 (9 H)
$[Fe(dmva)_3]^-$	$S(CD_3)_2O$	3.35 (9 H)	3.09 (9 H)
$[Fe(dmva)_3]^-$	$S(CD_3)_2O$ [c]	3.36 (9 H)	3.10 (9 H)
$[Ru(dmva)_3]^-$	$S(CD_3)_2O$	3.33 (9 H)	3.10 (9 H)
H_2va^-	$S(CD_3)_2O$	10.1 (2 H, vbr)	
$[Co(H_2va)_3]$	$S(CD_3)_2O$	13.1 (3 H, vbr)	11.57 (3 H)
$[Fe(H_2va)_3]^-$	$S(CD_3)_2O$	12.0 (3 H, vbr)	10.80 (3 H)
$[Ru(H_2va)_3]^-$	$S(CD_3)_2O$	11.93 (3 H, br)	10.7 (3 H)

[a] In p.p.m. downfield relative to $SiMe_4$ as internal standard, at 27 °C. [b] Recorded on a Perkin-Elmer B 24 B instrument. [c] At 60 °C.

TABLE 3

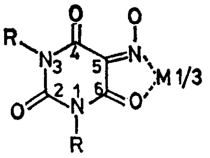
pK_a Values for deprotonation at 25 °C in 0.5 mol dm^{-3} NaCl

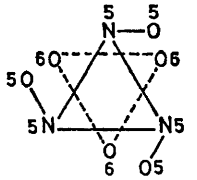
Compound	Deprotonation site	pK_a
H_2va^-	N(1) + N(3)	9.60 + 0.05
Hva^{2-}	N(1) + N(3)	13.4 ± 0.1
$[Co(H_2va)_3]$	N(1)	3.14 ± 0.1 *
$[Co(H_2va)_2(Hva)]^-$	N(1)	4.25 ± 0.05 *
$[Co(H_2va)(Hva)_2]^{2-}$	N(1)	5.21 ± 0.02 *
$[Co(Hva)_3]^{3-}$	N(3)	*ca.* 12
$[Fe(H_2va)_3]^-$	N(1)	5.2 ± 0.2
$[Fe(H_2va)_2(Hva)]^{2-}$	N(1)	6.35 ± 0.05
$[Fe(H_2va)(Hva)_2]^{3-}$	N(1)	7.54 ± 0.03
$[Fe(Hva)_3]^{4-}$	N(3)	
$[Ru(H_2va)_3]^-$	N(1)	5.96 ± 0.03
$[Ru(H_2va)_2(Hva)]^{2-}$	N(1)	7.05 ± 0.02
$[Ru(H_2va)(Hva)_2]^{3-}$	N(1)	7.93 ± 0.04
$[Ru(Hva)_3]^{4-}$	N(3)	*ca.* 13.3

* After fitting procedure from the pK_a values given in ref. 13.

in $[H_3O][Ru(H_2va)_3]\cdot 3H_2O$ [16] and in $[NH_4][Fe(H_2va)_3]\cdot 4.5H_2O$.[14]

The ^1H n.m.r. spectra of the ketoxime complexes are summarized in Table 2. All the spectra display two sharp signals. No coalescence is observed in the temperature range allowed by the solubility of the compounds in the solvents used. The fact that the n.m.r. spectra of the *N*-methyl derivatives of the ketoximate complexes display only two signals reveals three equivalent co-ordinated heterocycles; these spectra are in good agreement with an octahedral arrangement in a facial configuration in solution. The signal at lowest field is assigned to N(1)–Me and the second one to N(3)–Me. The spectrum of $Na[H_2va]$ exhibits only one very broad signal, due to rapid exchange between the two protons of the non-equivalent N(1) and N(3) sites in the heterocycle.[6] This broad signal splits into two peaks of equal intensity at lower fields as a result of the bidentate co-ordination of H_2va^- in $[M(H_2va)_3]^{n-}$ ($n = 0, M = Co^{III}$; $n = 1, M = Fe^{II}$ or Ru^{II}). By analogy with the ^1H n.m.r. spectra of other ketoximates and related complexes,[17,18] the broad peak at lowest field is assigned to the three equivalent N(1)–H protons and the sharp signal at highest field to the three equivalent N(3)–H protons. The breadth decreases from Co to Fe to Ru; $S(CD_3)_2O$ is found to be the best solvent to obtain resolved ^1H n.m.r. peaks. Unfortunately, it is not possible to obtain good ^1H n.m.r. spectra of the isolated complexes $[Co^{III}(Hva)_3]^{3-}$ [13] and $[Ru^{II}(Hva)_3]^{4-}$; indeed the solubility of the monohydrogenviolurate complexes is too low in all the solvents used.





In water it is possible to reversibly deprotonate the dihydrogenviolurate complexes. The protonation equilibria can be observed spectrally by the shifts of the visible-range bands as well as smaller changes in the rest of the spectrum (Figures 1—3). These spectral differences can be used to determine the acidity constants of the complexes; pK_a values for the loss of one proton from the dihydrogenviolurate complexes are listed in Table 3. The three first deprotonations which occur in the same pH range for the dihydrogenviolurate complexes are attributed to the N(1)–H sites, from comparison with the ^1H n.m.r. data. Measurements of the pK_a of deprotonations on the N(3)–H sites are vitiated by irreversible decomposition of these complexes at high pH. However, it is possible to place a lower limit on the pK_a values of these complexes (Table 3). The cobalt(III) and ruthenium(II) complexes are inert towards substitution [19,20] and this facilitates their isolation and systematic study. Unfortunately, the iron(II) complexes are not inert towards substitution [21] in water and it is necessary to add an excess of free ligand to prevent the dissociation of the complex, particularly in an acidic medium.

In all cases the co-ordination of dihydrogenviolurate to Co^{III}, Fe^{II}, and Ru^{II} markedly increases the acidity of the deprotonation sites N(1) and N(3) of the heterocycle compared with that of the deprotonation sites of the free H_2va^-. This effect is most marked for the N(1) position where the first ionization constant of the cobalt(III) complex is increased by a factor of 10^6 compared with that of the free H_2va^-. The acidity is enhanced by a factor of *ca.* 3×10^4 for $[Fe(H_2va)_3]^-$ and for the ruthenium(II) complex the increase in acidity is less, 3×10^3. The deprotonation constants of both $[Co(H_2va)_3]$ [13] and the corresponding 2-thiodihydrogenviolurato-complex [22] have been determined previously by potentiometry and are in good agreement with our results.

It should be noted that the deprotonated species of the dihydrogenviolurate, as well as the 2-thiodihydrogenviolurate, complexes are present in aqueous solution, even at low pH. This effect must be taken into account for the determination of the stability constants of the corresponding complexes, and the numerous determinations previously performed, which neglected this feature, must only be regarded as more or less good approximations.

The u.v.–visible spectra of the ketoximate complexes are

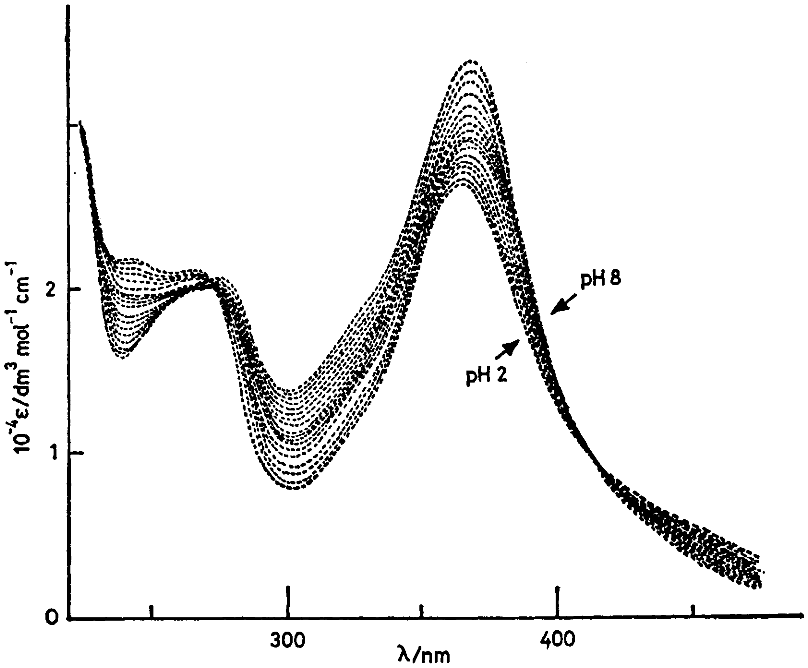


FIGURE 1 Electronic absorption spectral changes resulting from pH changes in a 1.17×10^{-4} mol dm^{-3} aqueous solution of $[Co(H_2va)_3]$; $I = 0.5$ mol dm^{-3} (NaCl), 25 °C

summarized in Table 4. The spectra of the *N*-methyl derivatives are remarkably similar to those of the N–H derivatives. These spectra exhibit an intense band in the u.v. region with a second broad visible absorption. The position of the first band and its intensity are similar to those observed for the free ligands, implying that this transition is essentially localized on the ligand and is presumably analogous to the $\pi \rightarrow \pi^*$ absorption seen for the free ligand. The spectra of the ruthenium complexes in water exhibit a supplementary absorption at 220 nm; the corresponding absorption is detected in the spectra of $[Co(H_2va)_3]$ and also in the spectra of the free ligands. This absorption, attributed to a $\pi \rightarrow \pi^*$ transition, is not however evident for the other complexes, the higher-energy transition being obscured by the excess of solvent or ligand. The broad absorption centred around 606 nm for the iron(II) and 495 nm for the ruthenium(II) complexes is assigned to a $d \rightarrow \pi^*$ transition from a comparison with corresponding di-imine complexes.[23] The interpretation of the spectra of the cobalt(III) complexes is not so simple; the broad absorption centred around 370 nm may be assigned to a $\pi \rightarrow d$ [19] transition. The visible bands are very sensitive to the solvent. The calculated spectra of the deprotonated derivatives of the H_2va^- complexes are obtained from the

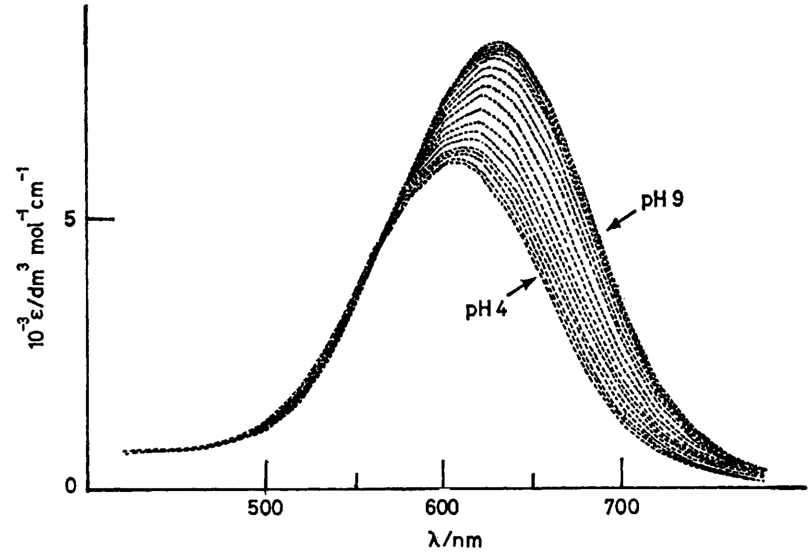


FIGURE 2 Electronic absorption spectral changes resulting from pH changes in a 2.84×10^{-4} mol dm^{-3} aqueous solution of $Na[Fe(H_2va)_3]$ with 3×10^{-2} mol dm^{-3} $Na[H_2va]$, after correction for the absorption of the $Na[H_2va]$ at the corresponding pH; $I = 0.5$ mol dm^{-3} (NaCl), 25 °C

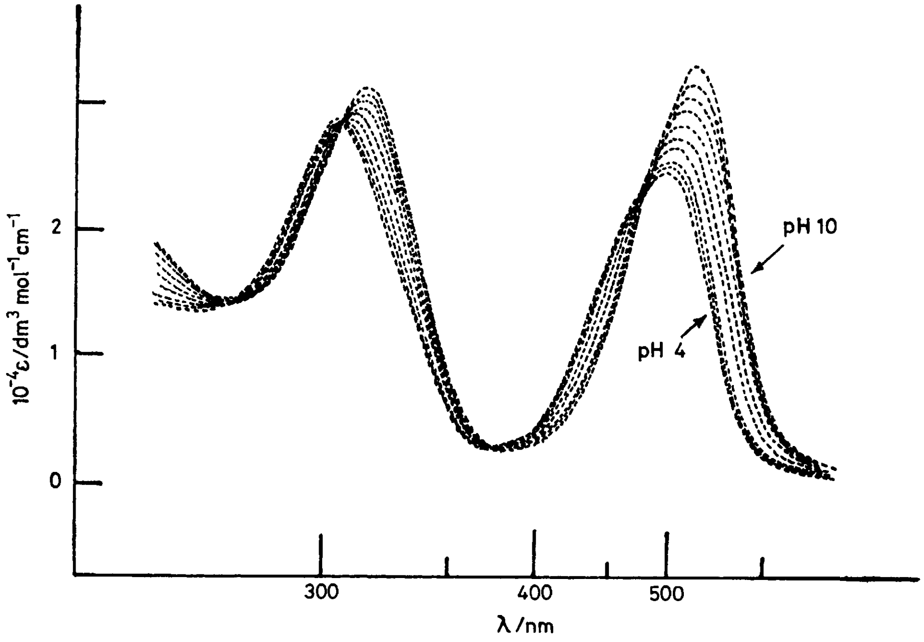


FIGURE 3 Electronic absorption spectral changes resulting from pH changes in a 2.7×10^{-4} mol dm^{-3} aqueous solution of $Na[Ru(H_2va)_3]$; I = 0.5 mol dm^{-3} (NaCl), 25 °C

TABLE 4

Electronic spectra of ketoxime complexes at 25 °C

Compound	$\lambda_{max.}$/nm [a] H_2O + 0.5 mol dm^{-3} NaCl	 MeCN	Tentative assignment
Hdmva	253 (16 400)	260 (7 000)	$\pi \rightarrow \pi^*$
$dmva^-$	222 (14 200)		$\pi \rightarrow \pi^*$
	314 (17 200)	316 (8 900)	$\pi \rightarrow \pi^*$
	535 (48)	640 (60)	$n \rightarrow \pi^*$
$[Co(dmva)_3]$		273 (15 000)	$\pi \rightarrow \pi^*$
		372 (22 000)	
		315 (16 000)	$\pi \rightarrow \pi^*$
$[Fe(dmva)_3]^-$		606 (7 000)	$d \rightarrow \pi^*$
$[Ru(dmva)_3]^-$	222 (27 500)		$\pi \rightarrow \pi^*$
	307 (17 500)	306 (12 500)	$\pi \rightarrow \pi^*$
	495 (16 000)	478 (9 700)	$d \rightarrow \pi^*$
H_3va	250 (12 500)		$\pi \rightarrow \pi^*$
H_2va^-	220 (1 500)		$\pi \rightarrow \pi^*$
	310 (13 500)		$\pi \rightarrow \pi^*$
	540 (50)		$n \rightarrow \pi^*$
$[Co(H_2va)_3]$ [b]	220 (36 000)		$\pi \rightarrow \pi^*$
	265 (23 000)		$\pi \rightarrow \pi^*$
	365 (27 000)		
$[Co(H_2va)_2(Hva)]^-$ [b]	268 (22 000)		$\pi \rightarrow \pi^*$
	367 (29 500)		
$[Co(H_2va)(Hva)_2]^{2-}$ [b]	272 (20 000)		$\pi \rightarrow \pi^*$
	368 (29 800)		
$[Co(Hva)_3]^{3-}$ [b]	222 (32 000)		$\pi \rightarrow \pi^*$
	277 (21 400)		$\pi \rightarrow \pi^*$
	369 (34 000)		
$[Fe(H_2va)_3]^-$ [b]	605 (6 000)		$d \rightarrow \pi^*$
$[Fe(H_2va)_2(Hva)]^{2-}$ [b]	610 (5 200)		$d \rightarrow \pi^*$
$[Fe(H_2va)(Hva)_2]^{3-}$ [b]	620 (7 000)		$d \rightarrow \pi^*$
$[Fe(Hva)_3]^{4-}$ [b]	635 (8 500)		$d \rightarrow \pi^*$
$[Ru(H_2va)_3]^{3-}$ [b]	220 (32 000)		$\pi \rightarrow \pi^*$
	303 (28 000)		$\pi \rightarrow \pi^*$
	495 (24 800)		$d \rightarrow \pi^*$
$[Ru(H_2va)_2(Hva)]^{2-}$ [b]	498 (27 200)		$d \rightarrow \pi^*$
$[Ru(H_2va)(Hva)_2]^{3-}$ [b]	504 (30 900)		$d \rightarrow \pi^*$
$[Ru(Hva)_3]^{4-}$ [b]	224 (33 000)		$\pi \rightarrow \pi^*$
	310 (29 400)		$\pi \rightarrow \pi^*$
	515 (33 200)		$d \rightarrow \pi^*$

[a] Values of $\epsilon_{max.}$/dm^3 mol^{-1} cm^{-1} are given in parentheses. [b] Resolved species spectra obtained from the experimental spectra of Figures 1—3.

spectrophotometric data after a fitting procedure with the best pK_a values (Tables 3 and 4). The removal of one proton from the co-ordinated H_2va^- at the N(1)–H site causes changes in all the bands. The u.v. band shifts to lower energy and increases in intensity whereas the visible band shifts to lower energy only for the iron and ruthenium complexes, although the intensity increases for all the complexes. The removal of one proton from the heterocycle at the N(3)–H site causes similar changes; the u.v. and visible absorptions shift to lower energies and increase in intensity. However, in these strongly basic solutions, the complex degrades by a rapid and irreversible decomposition to unknown products. The free ligands H_2va^- and $dmva^-$ are purple in water and violet in acetonitrile or dimethyl sulphoxide. These colours correspond to a low-energy absorption band which has been assigned to a $n \rightarrow \pi^*$ transition by comparison with the low-energy absorption band of nitrosoarenes and by the sensitivity of this transition to the nature of the solvent.[24,25]

DISCUSSION

From the i.r. and ^{1}H n.m.r. results of the present work some conclusions can be put forward: the series of ketoximate complexes possesses the same structure either in the solid state or in solution. *X*-Ray crystallographic analyses of $[NH_4][Fe(H_2va)_3]\cdot4.5H_2O$,[14] $[H_3O][Ru(H_2va)_3]\cdot3H_2O$,[16] and $Ba[Ru(H_2va)_3]_2\cdot9H_2O$ [26] show that the metal binds to the violurato-ligands at N(5) and O(6) forming a five-membered chelate ring, the disposition of the ligands around the metal being *fac*. The same structure has been suggested on the basis of i.r. data for the cobalt(III) complexes in the solid state. The origin of the predominance of the facial geometry found for all the complexes in the present work as for ketoximate,[27,28] nitrosophenol,[29] and nitroso-oximate [30] tris chelates cannot be attributed to a steric effect. The overlap between the orbitals on the metal and the π system of the ligands should provide the greatest stability in the *fac* configuration. The ^1H n.m.r. data indicate that the three violurate ligands are equivalent in all the complexes of the present work. This is in accordance with the *fac* configuration in solution. The complexes $[Co(H_2va)_3]$,[13] $[Co(dmva)_3]$, $[NH_4][Fe(H_2va)_3]$,[14] $Na[Fe(dmva)_3]$, $Na[Ru(H_2va)_3]$,[6] and $Na[Ru(dmva)_3]$ [6] were found to be diamagnetic at room temperature suggesting a low-spin d^6 octahedral configuration for all the complexes. The low-spin character of all the complexes studied in the present work suggests that the violurate anions are very strong-field ligands as are most ketoximate ligands.

In the solid state, the hydrogen atoms of the compound $[H_3O][Ru(H_2va)_3]\cdot 3H_2O$ have been located at the N(1) and N(3) sites of the heterocycle.[16] However, it is possible that tautomerism [31,32] exists in solution particularly for the protons of the N(1) sites with O(2) sites and would be in accordance with the broad signal observed in the ^1H n.m.r. spectra of the complexes $[M(H_2va)_3]^{n-}$ ($n = 0$ or 1). Proton chemical shifts have been shown to be related to the electron density of the carbon atoms to which the hydrogen atom is bound in aromatic molecules.[33] Heterocycles, however, elude such a straightforward interpretation due to the anisotropy introduced by the heteroatoms.[11] Investigations of chemical shifts in ^1H n.m.r. spectra of a series of related complexes of H_2va^- and $dmva^-$ lead to several conclusions. Table 3 gives ^1H n.m.r. shifts of complexed H_2va^- and $dmva^-$ relative to the free anions in $S(CD_3)_2O$. The downfield shifts are due particularly to the polarity of the $H^{\delta+}{-}N^{\delta-}$ or $H_3C{-}N$ bonds caused by complexation. They are more sensitive for the N(1) than for the N(3) sites and decrease from Co^{III} to Fe^{II} to Ru^{II} and are evidence for electron-density depletion.

The co-ordination of the metal to the O(6) and N(5) atoms of the heterocycle has a profound effect on the acidity of the dihydrogenviolurate. The acidity of the N(1) sites nearest to the metal is increased by a factor of 10^6 for the first dissociable proton of $[Co(H_2va)_3]$, while the ionization constants of protons at N(3) sites are increased by a factor of *ca.* 10. Co-ordination to iron(II) enhances the acidity of H_2va^- at N(1) sites by a factor of *ca.* 10^4 but co-ordination to Ru^{II} by a factor of 10^3. These results are in good agreement with the ^1H n.m.r. data. Electrostatic considerations might predict that deprotonation would be facilitated in the cobalt(III) complex by the high charge of the metal centre. The difference between the acidity of the N(1) sites of Fe^{II} and Ru^{II} is consistent with back donation of a considerable amount of electron density from ruthenium(II) in the π system of the violurate ligand. When a competitive ligand for π-back bonding, such as a nitrosyl, is introduced into the co-ordination sphere of ruthenium the acidity of the N(1) and N(3) sites increases again by at least a factor of 5×10^3, as was demonstrated previously [12] for $[Ru(H_2va)_2(NO)Cl]$.

The stabilization of Ru^{II} relative to Fe^{II} evidenced by electronic spectroscopy is assumed to be attributed to π-back bonding. The visible spectra of free H_2va^- or $dmva^-$ exhibit one weak absorption band at low energy. This band is assigned to a $n \rightarrow \pi^*$ transition and is consistent with a low-lying π^* system which may be accessible for back bonding. The absorption bands near 220 nm for H_2va^- or $dmva^-$, either free or bound to the metal, are close in energy. The higher-energy $\pi \rightarrow \pi^*$ transition in the ligand is not perturbed by chelation. The lower-energy $\pi \rightarrow \pi^*$ transition in free H_2va^- or $dmva^-$ shifts to higher energy when it is bound to the metal and when it is protonated at the O(5) site, particularly for Co^{III} and H^+. This shift is assumed to show the loss, at least partial, of π delocalization which occurs with complexation by Co^{III} or protonation at the O(5) site.

For the H_2va complexes, the deprotonations of the co-ordinated heterocycle in $[Co(H_2va)_3]$ result in only very small changes in energy of the electronic transitions. These features point to an analogous stabilization of the complex when it is protonated or deprotonated. In contrast, the progressive deprotonations of $[Fe(H_2va)_3]^-$ and $[Ru(H_2va)_3]^-$ exhibit gradual shifts to lower energies for the $\pi \rightarrow \pi^*$ transition and particularly for the $d \rightarrow \pi^*$ transition. These observations indicate changes in the energy levels of the complexes and suggest that the deprotonated complexes are more stable.

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