Novel Ruthenium Nitrosyl Complexes formed by Nitrosating the Tris-(violurato)- and Tris(1,3-dimethylviolurato)-ruthenate(II) Anions

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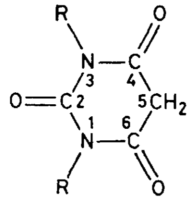
The salt $Na_2[Ru(NO)(NO_2)_4(OH)]$ reacts with barbituric acid in water to give $Na[Ru(H_2va)_3]$ (H_2va^- = bidentate violurate), and with 1,3-dimethylbarbituric acid to give $Na[Ru(dmva)_3]$ ($dmva^-$ = bidentate 1,3-dimethylviolurate). The complexes react with $Na[NO_2]$ in acidic aqueous solutions to afford a series of novel diamagnetic nitrosylruthenium complexes of the general type *cis*-$[Ru(L{-}L)_2(NO)X]$ (L–L = bidentate H_2va^- or $dmva^-$; X^- = Cl^-, Br^-, or unidentate H_2va^- or $dmva^-$). In water, acetonitrile, or dimethyl sulphoxide, the complexes *cis*-$[Ru(L{-}L)_3(NO)]$ release the co-ordinated nitrosyl ligand owing to the intramolecular transformation: *cis*-[Ru(L–L)$_2$(NO)(unidentate L–L)] → [Ru(L–L)$_2$(bidentate L–L)]$^-$ + $[NO]^+$. On the basis of the i.r. and ^1H n.m.r. spectra, the most probable structures of the complexes are given and the high electrophilicity of co-ordinated NO is shown to result from the strong π-backbonding properties of the bidentate violurate ligands.

MOST of the known nitrogen monoxide complexes of ruthenium are of the general type $[Ru(NO)L_5]$, in which the terminal Ru(NO) group is linear or approximately linear and can be considered *formally* to involve essentially Ru^{II} and $[NO]^+$ with appreciable π back donation from ruthenium to nitrosyl.[1-4] In these octahedral complexes the reactivity of the co-ordinated nitrosyl group is dependent on the nature of the other ligands L attached to ruthenium.[5-7] In most complexes where L = Cl, Br, I, OH, H_2O, NH_3, or any other 'hard' base, the Ru(NO) group remains intact through a variety of substitution reactions with many different bases under various conditions.[2,8,9] However, it has been shown recently that a few complexes which contain more than two π-acceptor ligands L in addition to NO itself {*e.g.* $[Ru(NO)(CN)_5]^{2-}$, $[Ru(NO)(das)_2Cl]^{2+}$ (das = 1,2-dimethylarsinobenzene), and $[Ru(NO)(bipy)_2Cl]^{2+}$ (bipy = 2,2′-bipyridyl)} may be attacked at the co-ordinated nitrosyl by nucleophiles such as ammonia, hydrazines, 'activated' arylamines, hydroxylamine, azide, and hydroxide ions.[5-7, 10-13]

Very recently, the first example was reported[14] of a reaction between co-ordinated nitrosyl and a β-diketone to give a bidentate ketone oxime[15] ligand bound to ruthenium, and we reported[16] the formation of the complexes tris(violurato)ruthenate(II), $[Ru(H_2va)_3]^-$, and tris(1,3-dimethylviolurato)ruthenate(II), $[Ru(dmva)_3]^-$, by the reactions of $[Ru(NO)(NO_2)_4(OH)]^{2-}$ with the following 1*H*,3*H*,5*H*-pyrimidine-2,4,6-triones:



R
H : barbituric acid (H_2ba)
Me : 1,3 - dimethylbarbituric acid (Hdmba)

In these cases, both the co-ordinated nitrosyl and nitrite groups react with the active methylene site of the pyrimidines to give the corresponding 5-oxime derivatives which act in their deprotonated form (H_2va^- and $dmva^-$) as bidentate ligands *via* the oxime-nitrogen atom N^7 and the carbonyl-oxygen atom O^8, as shown by a recent *X*-ray study.[17] We have also briefly reported[16a] novel nitrosylruthenium complexes formed by nitrosating $[Ru(H_2va)_3]^-$ with sodium nitrite in acidic solutions. This method appears to be one of the ways[18] of introducing the nitrosyl group into the co-ordination sphere

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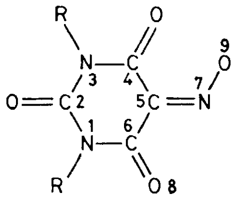
of a ruthenium atom already linked to three strong π-acceptor chelate ligands.



R
H: violuric acid (H_3va)
Me: 1,3-dimethylvioluric acid (Hdmva)

This paper describes in greater detail the preparations, characterizations, and properties of a series of nitrosyl (^{14}NO and ^{15}NO) complexes of the type *cis*-$[Ru(L-L)_2(NO)X]$ (L–L = H_2va or dmva; X = Cl, Br, or unidentate L–L) as well as those of the starting complexes $[Ru(L-L)_3]^-$. Special emphasis is placed on the discussion of the i.r. and n.m.r. spectra in terms of the mutual influences between the $[NO]^+$, L–L, and X^- ligands.

EXPERIMENTAL

Starting Materials and Analysis.—The salt $Na_2[Ru(NO)(NO_2)_4(OH)]\cdot 2H_2O$ was obtained as described previously.[19] The water of crystallization was removed by prolonged drying *in vacuo* over P_4O_{10}. Barbituric acid and 1,3-dimethylbarbituric acid were purchased from E. Merck (Germany). The isotopically substituted compounds (^{15}NO) were prepared from sodium nitrite $Na[^{15}NO_2]$ (96.3%) which was purchased from Merck, Sharp, and Dohme (Canada). The chemicals were of reagent grade and were not further purified. The elemental analyses (C, H, N, Na, Cl, and Br) were by the Service Central de Microanalyse (Centre National de la Recherche Scientifique, Thiais, France). Ruthenium was determined as described previously.[16b]

Physical Measurements.—The ^1H n.m.r. spectra of the products dissolved in $(CD_3)_2SO$ were recorded at *ca.* 37 °C on a Brücker WH 90 spectrometer with $SiMe_4$ as internal reference. The i.r. spectra were obtained on a Beckman IR 12 spectrometer in the 400—4 000 cm^{-1} region (KBr discs or Nujol mulls between CsI plates) and on a Polytec FIR 30 spectrometer in the 50—420 cm^{-1} region (polyethylene discs). The electronic spectra of the products dissolved in acetonitrile were recorded on a Jobin–Yvon DF 170 spectrophotometer. Magnetic-susceptibility measurements were made using the Faraday technique.

Preparation of the Complexes.—All the syntheses were carried out in darkness under an argon atmosphere. The yields are based on the ratio of the ruthenium in the product to that in the starting material.

Sodium tris(1,3-dimethylviolurato)ruthenate(II). A sample of $Na_2[Ru(NO)(NO_2)_4(OH)]$ (2 g, 5 mmol) was dissolved in an aqueous solution (100 cm^3) containing 1,3-dimethylbarbituric acid (3.9 g, 25.2 mmol). The solution was warmed at 40 °C for 5 h. It became deep red and a red precipitate quickly appeared. After cooling, the red solid was filtered off, washed twice with ice water and with ethanol, and dried at 150 °C under argon; yield 92% (Found: C, 31.75; H, 3.90; N, 18.5; Na, 3.35; Ru, 14.7. Calc. for $C_{18}H_{18}N_9NaO_{12}Ru$: C, 31.95; H, 3.85; N, 18.6; Na, 3.40; Ru, 14.95%).

Sodium tris(violurato)ruthenate(II). A sample of $Na_2[Ru(NO)(NO_2)_4(OH)]$ (2 g, 5 mmol) was dissolved in an aqueous solution (100 cm^3) containing barbituric acid (3.32 g, 25.2 mmol). The solution was warmed at 40 °C for 5 h, and it became deep red. After cooling to room temperature, a saturated solution of $Ba[NO_3]_2$ was added. A red product precipitated immediately, and was filtered off, washed several times with small portions of water, and dried in air. A sample (0.5 g) of the product was suspended in water (100 cm^3) with Dowex W 50 ion-exchange resin in the Na^+ form (10 g). After vigorous stirring the suspension dissolved, the resin was separated by filtration, and the solution was concentrated over P_4O_{10}. The small red crystals which appeared were filtered off, washed with ice water, recrystallized from water, and then completely dehydrated at 150 °C under argon; yield 80% (Found: C, 24.0; H, 0.95; N, 21.3; Na, 3.80; Ru, 17.0. Calc. for $C_{12}H_6N_9NaO_{12}Ru$: C, 24.3; H, 1.00; N, 21.25; Na, 3.90; Ru, 17.05%).

Tris(1,3-dimethylviolurato)nitrosylruthenium. A sample of $Na[Ru(dmva)_3]$ (0.4 g, 0.6 mmol) was dissolved in water (1 l) with sodium nitrite (0.05 g, 0.72 mmol). Perchloric acid was added until pH 1.5. A yellow product precipitated slowly and the solution became colourless. The product was filtered off, washed with cold water, and dried *in vacuo* over P_4O_{10}; yield 99% (Found: C, 31.6; H, 3.45; N, 20.6; Ru, 14.65. Calc. for $C_{18}H_{18}N_{10}O_{13}Ru$: C, 31.6; H, 3.20; N, 20.5; Ru, 14.8%). The same procedure was used to prepare $[Ru(dmva)_3(^{15}NO)]$.

Nitrosyltris(violurato)ruthenium. The procedure was the same as for $[Ru(dmva)_3(NO)]$, except that $Na[Ru(H_2va)_3]$ was the starting complex; yield 80% (Found: C, 23.5; H, 1.3; N, 22.8; Ru, 16.3. Calc. for $C_{12}H_6N_{10}O_{13}Ru$: C, 24.0; H, 1.0; N, 23.3; Ru, 16.8%). The same procedure was also used to prepare $[Ru(H_2va)_3(^{15}NO)]$.

Chlorobis(1,3-dimethylviolurato)nitrosylruthenium. A sample of $Na[Ru(dmva)_3]$ (0.2 g, 0.30 mmol) was suspended in degassed 4 mol dm^{-3} hydrochloric acid (50 cm^3). Sodium nitrite (0.024 g, 0.35 mmol) was added quickly and the suspension was stirred until a clear yellow solution was obtained. A yellow product precipitated in a few minutes. It was filtered off, washed several times with small portions of cold water and ethanol, and dried *in vacuo* over P_4O_{10}; yield 90% (Found: C, 27.0; H, 2.25; Cl, 6.85; N, 18.45; Ru, 18.7. Calc. for $C_{12}H_{12}ClN_7O_9Ru$: C, 26.95; H, 2.25; Cl, 6.65; N, 18.35; Ru, 18.9%). The same procedure was used to prepare $[Ru(dmva)_2(^{15}NO)Cl]$.

Bromobis(1,3-dimethylviolurato)nitrosylruthenium. The procedure was the same as for $[Ru(dmva)_2(NO)Cl]$, except that a 4 mol dm^{-3} hydrobromic acid solution was used instead of HCl; yield 90% (Found: C, 24.85; H, 2.10; Br, 14.1; N, 16.75; Ru, 17.2. Calc. for $C_{12}H_{12}BrN_7O_9Ru$: C, 24.85; H, 2.05; Br, 13.8; N, 16.95; Ru, 17.45%). The same procedure was used to prepare $[Ru(dmva)_2(^{15}NO)Br]$.

Chloronitrosylbis(violurato)ruthenium. A sample of $Na[Ru(H_2va)_3]$ (0.5 g, 0.85 mmol) was dissolved in degassed 3 mol dm^{-3} HCl (100 cm^3). Sodium nitrite (0.12 g, 1.7 mmol) was added quickly. The initial deep red solution became yellow. The temperature was held at 5 °C for a few days, after which small yellow crystals slowly appeared. They were filtered off, washed several times with small

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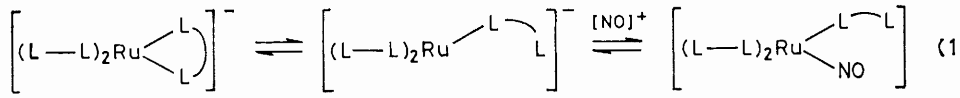
portions of ice water, and dried in air. They were completely dehydrated when dried *in vacuo* over P_4O_{10}; yield 65% (Found: C, 19.9; H, 1.1; Cl, 7.40; N, 20.5; Ru, 20.7. Calc. for $C_8H_4ClN_7O_9Ru$: C, 20.1; H, 0.85; Cl, 7.40; N, 20.5; Ru, 21.1%). The same procedure was used to prepare $[Ru(H_2va)_2(^{15}NO)Cl]$.

Bromonitrosylbis(violurato)ruthenium. The procedure was the same as for $[Ru(H_2va)_2(NO)Cl]$, except that 3 mol dm^{-3} HBr was used instead of HCl. The orange product was completely dehydrated when dried *in vacuo* over P_4O_{10}; yield 60% (Found: C, 17.8; H, 1.0; Br, 14.8; N, 18.2; Ru, 18.9. Calc. for $C_8H_4BrN_7O_9Ru$: C, 18.3; H, 0.75; Br, 15.2; N, 18.7; Ru, 19.3%). The same procedure was used to prepare $[Ru(H_2va)_2(^{15}NO)Br]$.

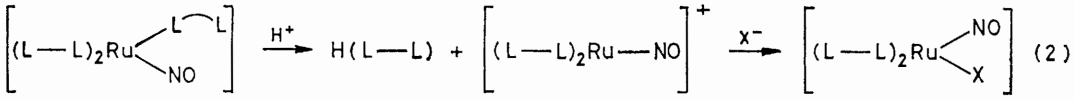
RESULTS AND DISCUSSION

Synthetic Studies.—From the reactions between $Na_2[Ru(NO)(NO_2)_4(OH)]$ (1 mol) and barbituric acid or 1,3-dimethylbarbituric acid (5 mol) in aqueous solution, deep red complexes $Na[Ru(H_2va)_3]$ and $Na[Ru(dmva)_3]$ were isolated in high yields (80—90%). The complexes are diamagnetic, which strongly supports their formulation as ruthenium(II) species. This is confirmed by their electronic spectra (see below) and by the existence of an analogous iron(II) complex,[20b] $Na[Fe(pdo)_3]$ (Hpdo = pentane-2,4-dione oxime). The complex $Na[Ru(H_2va)_3]$ obtained in this way is identical to the final product of direct complex formation between Ru^{III} and violurate in aqueous solution at pH 2—5.5.[16a,21] Different reactions leading to the formation of ketone oximato and analogous complexes of transition metals[15] have recently been reported: direct reaction of Hpdo with metal salts,[20] reaction of co-ordinated β-diketonate or analogous ligands with NO (refs. 22 and 23) or with both nitrite and ammonium ions,[24] and reaction of pentane-2,4-dione with co-ordinated nitrite[23] or with co-ordinated nitrosyl.[14] However, no reaction between β-diketone and *both* nitrosyl and nitrite co-ordinated at the same metal has yet been reported. The preparations of the complexes $Na[Ru(L\text{-}L)_3]$ reported here appear to be the first examples of the latter reaction.

From the reactions between $Na[Ru(L\text{-}L)_3]$ and a slight excess of sodium nitrite ($[NO_2]^- : Ru = 1.2$—$2 : 1$) in acidic aqueous solutions, a series of novel diamagnetic ruthenium(II) nitrosyl (^{14}NO and ^{15}NO) complexes of the type *cis*-$[Ru(L\text{-}L)_2(NO)X]$ (X = Cl, Br, or unidentate L-L) were isolated in almost quantitative yields with respect to ruthenium when L-L = $dmva^-$, and in lower yields (60—80%) when L-L = H_2va^-. The nature of these complexes is dependent on the nature and concentration of the acid used. At pH 1.5 nitrosation by $[NO_2]^-$-H^+ leads to the formation of a yellow product of composition $[Ru(L\text{-}L)_3(NO)]$ within a few minutes, whatever the acid used ($HClO_4$, H_2SO_4, HCl, HBr, *etc.*). From the i.r. and ^1H n.m.r. spectra (see below), it is clear that the complexes $[Ru(L\text{-}L)_3(NO)]$ contain two bidentate L-L ligands and one unidentate L-L ligand *cis* to the nitrosyl group, giving an octahedral structure, as found by *X*-ray diffraction in the complex $[Ru(NO)(S_2CNEt_2)_3]$.[25] If the nitrosation is performed in 3—4 mol dm^{-3} HCl or HBr, the ultimate yellow-orange product of the reaction has the composition $[Ru(L\text{-}L)_2(NO)X]$ (X = Cl or Br). Again the ligand X is *cis* to the NO group, as shown below. The *cis* configuration of all these nitrosyl complexes might be a direct result of the mechanism of their formation. Indeed, a spectrophotometric study of the kinetics of nitrosation of $[Ru(L\text{-}L)_3]^-$ by $[NO_2]^-$-H^+ shows[16a,26] that nitrosyl complex formation must take place by direct nitrosonium ion ($[NO]^+$) attack at ruthenium at the sixth co-ordination site left free by *prior* opening of one chelate ring, the resulting product being *cis*-$[Ru(L\text{-}L)_3(NO)]$ at pH 1.5 [equation (1)]. If the solution is made more acidic with 3—4 mol dm^{-3} HCl or HBr, the unidentate L-L ligand of the above complex is liberated by acid-catalyzed halogenation to give the final product *cis*-$[Ru(L\text{-}L)_2(NO)X]$ (X = Cl or Br) [equation (2)].



(1)



(2)

It has been postulated previously[7,27] that attack of $[NO]^+$, generated by acidic solutions of nitrite salts, on ruthenium complexes occurs in reactions (3) [L-L = 2,2'-

$$[Ru(L\text{-}L)_2(OH_2)X]^+ \xrightarrow{[NO_2]^- \text{-} H^+} H_2O + [Ru(L\text{-}L)_2(NO)X]^{2+} \quad (3)$$

bipyridyl (bipy) or 1,10-phenanthroline (phen)][7] and (4),[27] with concomitant displacement of co-ordinated H_2O or NH_3. The reaction $[Ru^{II}(L\text{-}L)_3]^- \xrightarrow{[NO_2]^- \text{-} H^+}$

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[20] (*a*) N. J. Patel and B. C. Haldar, *J. Inorg. Nuclear Chem.*, 1967, **29**, 1037; U. B. Talwar and B. C. Haldar, *ibid.*, 1970, **32**, 213; (*b*) A. V. Ablov and V. N. Zubarev, *Russ. J. Inorg. Chem.*, 1968, **13**, 1563; (*c*) K. S. Bose, B. C. Sharma, and C. C. Patel, *Inorg. Chem.*, 1973, **12**, 120.

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[26] S. Sueur, C. Bremard, and G. Nowogrocki, unpublished work.

[27] F. M. Lever and A. R. Powell, *J. Chem. Soc.* (*A*), 1969, 1477.

$[Ru^{II}(L{-}L)_3(NO)]$ reported here is an example of direct $[NO]^+$ attack at ruthenium with opening of one chelate ring. The mechanism of reaction (5) (R = Me, Et, or Bu^n) reported in 1938 [28] has not been studied, but it also involves opening of one chelate ring. However, in this case, there is also an *overall* redox process, Ru^{III} + NO $\longrightarrow$ $Ru^{II}(NO)$, which does not occur in our case. Indeed, oxidation of the metal by $[NO]^+$ or HNO_2, followed by reductive nitrosylation by NO, a mechanism which has been reported by other workers,[29] is not observed here because the rate of electron transfer is slower than that of nitrosation.[26]

$$[Ru(NH_3)_6]^{2+} \xrightarrow{[NO_2]^- - H^+} NH_3 + [Ru(NO)(NH_3)_5]^{3+} \quad (4)$$

$$[Ru^{III}(S_2CNR_2)_3] + NO(g) \longrightarrow [Ru^{II}(NO)(S_2CNR_2)_3] \quad (5)$$

Behaviour of the Complexes in Solution.—The tris(chelate) complexes $Na[Ru(L{-}L)_3]$ are soluble and stable in water (*ca.* 10^{-2} mol dm^{-3} if L–L = H_2va^-, *ca.* 5×10^{-3} mol dm^{-3} if L–L = dmva$^-$) and in the usual polar organic solvents methanol, ethanol, nitromethane, dimethylformamide (dmf), acetonitrile, and dimethyl sulphoxide, the latter (dmso) being the best solvent. In contrast, the nitrosyl complexes are only slightly soluble (L–L = H_2va^-) or almost totally insoluble (L–L = dmva$^-$) in water (pH <2), MeOH, and EtOH. Their solvolysis in alcohols does *not* lead to the formation of alkyl nitrites.[30] Except for nitromethane, the aprotic organic solvents mentioned above (dmf, MeCN, and dmso) are reasonably good inert [31] solvents for all the nitrosyl derivatives. However, in neutral water, MeCN, or dmso the complexes $[Ru(L{-}L)_3(NO)]$ lose their $[NO]^+$ ligand and regenerate $[Ru(L{-}L)_3]^-$ within a few minutes. This transformation has been observed in $(CD_3)_2SO$ from the ^1H n.m.r. spectra and in MeCN from the u.v.–visible absorption spectra (see below).

Spectral Studies.—*Electronic spectra.* The u.v.–visible absorption spectra of some of the complexes studied have been given previously.[32] In acetonitrile, all the complexes show an intense absorption at 320 nm ($\varepsilon \simeq 3 \times 10^4$ dm^3 mol^{-1} cm^{-1}) assigned to an internal-ligand transition of the type $\pi \rightarrow \pi^*$. In addition, the spectra of $[Ru(L{-}L)_3]^-$ exhibit another absorption at 495 nm ($\varepsilon \simeq 2.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}) due to the 'inverted' $t_{2g}(Ru) \rightarrow \pi^*(L{-}L$ ligand) electron-transfer transition (metal-to-ligand charge transfer),[33-35] and the nitrosyl complexes gave a strong shoulder at 360 nm assigned to a $d_\pi(Ru) \rightarrow \pi^*(NO)$ transition.[36]

When kept in darkness, acetonitrile solutions of the

TABLE 1

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

$Na[H_2va]$	$Na[Ru(H_2va)_3]$	*cis*-$[Ru(H_2va)_2(^{14}NO)Cl]$	*cis*-$[Ru(H_2va)_2(^{14}NO)Br]$	*cis*-$[Ru(H_2va)_3(^{14}NO)]$	Tentative assignments
		1 950vs	1 949vs 1 940 (sh)	1 924vs	$\nu(N{\equiv}O)$
1 743vs	1 735vs	1 790 (sh) 1 760vs	1 755vs 1 738vs	1 755 (sh) 1 739vs	$\nu(C^2{=}O)$
[a] 1 710vs 1 683vs	1 681vs	1 725 (sh) 1 706vs	1 726vs 1 702vs	1 705 (sh) 1 697vs	$\nu(C^4{=}O)$
1 572vs	1 595vs	1 615w 1 583vs	1 608w 1 578vs	1 610 (sh) 1 594vs	$\nu(C^5{=}N^7) + \nu(C{=}C)$
	1 505s	1 514s	1 514s	1 507s	$\nu(C^6{=}O^8)$
				1 381vs, 1 355w	Unidentate [b] $\nu(C^5{=}C^6)$ [c] + $\nu(N^7{=}O^9)$ [d]
1 145s	1 210m,br	1 227m	1 225s	1 245m	$\nu(N^7{-}O^9)$
				1 152m, 1 115s	Unidentate [b] $\nu(C^6{-}O^8)$ [e] + $\nu(C^5{-}N^7)$ [f]
		?	620 (sh)	641w	$\nu(Ru{-}NO)$
	612w	608m	605s	610m	$\nu(Ru{-}O^8) + \delta(Ru{-}NO)$
574s	594s	600m	596s	605 (sh)	? + $\delta(Ru{-}NO)$
				512m	Unidentate [b] $\nu(Ru{-}O^8)$
	480w	490w	484s	495w	$\nu(Ru{-}O^8) + \nu(Ru{-}N^7)$
	335m	334m	330m	335 (sh)	$\nu(Ru{-}N^7) + \nu(Ru{-}O^8)$
		320s			$\nu(Ru{-}Cl)$
	?	265m	277s	280s	$\nu(Ru{-}N^7)$
	240 (sh)	249 (sh)	250 (sh)	240 (sh)	δ(Ru–ligands)?
			240w		$\nu(Ru{-}Br)$
	170 (sh)	160m	157w	165vw	δ(Ru–ligands)?

s = Strong, m = medium, w = weak, sh = shoulder, and br = broad.

[a] $\nu(C^4{=}O) + \nu(C^6{=}O)$ for unco-ordinated H_2va^-. [b] See text and structure (II). [c] Ref. 42. [d] Ref. 41*a*. [e] Ref. 41*c*. [f] Ref. 41*b*.

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[28] L. Malatesta, *Gazzetta*, 1938, **68**, 195.

[29] J. N. Armor, H. A. Scheidegger, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 5928; A. Takenaka, Y. Sasada, T. Omura, H. Ogoshi, and Z. Yoshida, *Bull. Chem. Soc. Japan*, 1974, **47**, 308.

[30] C. A. Reed and W. R. Roper, *J.C.S. Dalton*, 1972, 1243.

[31] C. A. Olah, N. A. Overchuk, and J. C. Lapierre, *J. Amer. Chem. Soc.*, 1965, **87**, 5785.

[32] S. Sueur, C. Bremard, and G. Nowogrocki, *J. Inorg. Nuclear Chem.*, 1976, **38**, 2037.

[33] I. P. Evans, G. W. Everett, jun., and A. M. Sargeson, *J.C.S. Chem. Comm.*, 1975, 139.

[34] P. Ford, De F. P. Rudd, R. Gaunder, and H. Taube, *J. Amer. Chem. Soc.*, 1968, **90**, 1187.

[35] P. Krumholz, *Structure and Bonding*, 1971, **9**, 139; D. F. Mahoney and J. K. Beattie, *Inorg. Chem.*, 1973, **12**, 2561; A. M. Zwickel and C. Creutz, *ibid.*, 1971, **10**, 2395.

[36] P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, 1966, **87**, 3340.

complexes $[\mathrm{Ru(L{-}L)_2(NO)X}]$ ($\mathrm{X = Cl}$ or Br) do not change with time, in contrast to the case for $[\mathrm{Ru(L{-}L)_3(NO)}]$. Indeed, in the spectra of the latter the shoulder at 360 nm decreases rapidly within *ca.* 30 min whilst a band at 495 nm increases in intensity. This is indicative of the dissociation (6) which is not photochemically

$$[\mathrm{Ru(L{-}L)_3(NO)}] \rightleftharpoons [\mathrm{Ru(L{-}L)_3}]^- + [\mathrm{NO}]^+ \qquad (6)$$

initiated since it occurs in the absence of light. It will be discussed after n.m.r. results.

TABLE 2

Characteristic i.r. bands (cm^{-1}) of the 1,3-dimethylviolurato-complexes

Na[dmva]	$\mathrm{Na[Ru(dmva)_3]}$	*cis*-$[\mathrm{Ru(dmva)_2(^{14}NO)Cl}]$	*cis*-$[\mathrm{Ru(dmva)_2(^{14}NO)Br}]$	*cis*-$[\mathrm{Ru(dmva)_3(^{14}NO)}]$	Tentative assignments
		1 912vs 1 904vs	1 910vs 1 903vs	1 930vs 1 910 (sh)	$\nu(\mathrm{N{\equiv}O})$
1 727vs	1 717vs	1 740vs 1 735 (sh)	1 730vs	1 740vs 1 730vs	$\nu(\mathrm{C^2{=}O})$
a 1 710 (sh) 1 665vs	1 665vs	1 685vs 1 682vs	1 690vs 1 682vs	1 688 (sh) 1 678vs	$\nu(\mathrm{C^4{=}O})$
1 520w	1 561vs	1 575vs 1 555vs	1 560vs 1 550vs	1 567vs 1 550 (sh)	$\nu(\mathrm{C^5{=}N^7}) + \nu(\mathrm{C{=}C})$
	1 514vs	1 537vs 1 522vs	1 538vs 1 523 (sh)	1 537vs 1 519vs	$\nu(\mathrm{C^6{=}O^8})$
				1 470vs	Unidentate [b] $\nu(\mathrm{C^5{=}C^6})$ [c] + $\nu(\mathrm{N^7{=}O^9})$ [d]
1 235s	1 260s	1 254 s	1 256 s	1 254 s	$\nu(\mathrm{N^7{-}O^9})$
				1 225s, 1 164s	Unidentate [b] $\nu(\mathrm{C^6{-}O^8})$ [e] + $\nu(\mathrm{C^5{-}N^7})$ [f]
		629m	626w	627m	$\delta(\mathrm{Ru{-}NO})$
		610w	610vw	604w	$\nu(\mathrm{Ru{-}NO})$
		598w	?	592w	$\delta(\mathrm{Ru{-}NO})$
	543w,br	555m	553m	555 (sh)	$\nu(\mathrm{Ru{-}O^8})$
				473m	Unidentate [b] $\nu(\mathrm{Ru{-}O^8})$
	449m	443m	440m	448s	$\nu(\mathrm{Ru{-}O^8}) + \nu(\mathrm{Ru{-}N^7})$
		339s			$\nu(\mathrm{Ru{-}Cl})$
	321w	321w	310w	300m	$\nu(\mathrm{Ru{-}N^7}) + \nu(\mathrm{Ru{-}O^8})$
	275vw	260w	272m	269m	$\nu(\mathrm{Ru{-}N^7})$
			250w		$\nu(\mathrm{Ru{-}Br})$
	?	239w	237w	245 (sh)	$\delta(\mathrm{Ru{-}ligands})$?

[a–f] As in Table 1. More detailed spectra of the complexes in Tables 1 and 2 may be found in Supplementary Publication No. SUP 22137 (3 pp.). See Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index Issue.

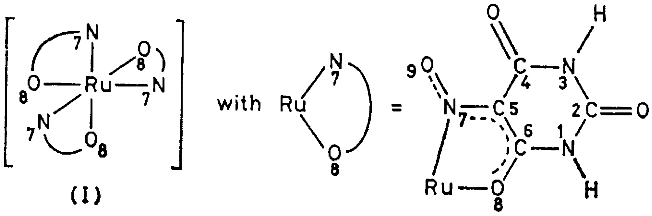
Infrared spectra. The tentative assignments of the characteristic vibrations of the violurato- and 1,3-dimethylviolurato-complexes (see Tables 1—3) are based on those reported for analogous nitrosyl (^{14}NO and ^{15}NO) and ketone oximato-complexes, and on the molecular structure of $\mathrm{H[Ru(H_2va)_3]{\cdot}4H_2O}$ which we have determined recently[17] by *X*-ray diffraction. The anion $[\mathrm{Ru(H_2va)_3}]^-$ has the ($\mathrm{N^7}$, $\mathrm{O^8}$) *cis–cis* (C_3) configuration (I) in which the pyrimidine and ruthenium chelate rings are nearly coplanar, and the two hydrogen atoms are located in a plane formed by the two rings, a structure which has also been found[37] in violuric acid $\mathrm{H_3va}$ and in $\mathrm{Rb[H_2va]}$ and $\mathrm{K[H_2va]{\cdot}2H_2O}$.[38] The interatomic distances in the rings are intermediate between single and double bonds, which indicates a strong π-electron delocalization in the bidentate violurate ligands.*

TABLE 3

Assignment of the Ru–N–O (^{14}N and ^{15}N) bands (cm^{-1})

	ν(NO)		ν(RuN)		δ(RuNO)	
Complex	^{14}N	^{15}N	^{14}N	^{15}N	^{14}N	^{15}N
cis-$[\mathrm{Ru(H_2va)_2(NO)Cl}]$	1950—	1914	*a*		*a*	
cis-$[\mathrm{Ru(H_2va)_2(NO)Br}]$	1949— 1940	1913	620	615	*b*	581
cis-$[\mathrm{Ru(H_2va)_3(NO)}]$	1924—	1889	641	637	*a*	
cis-$[\mathrm{Ru(dmva)_2(NO)Cl}]$	1912— 1904—	1875 1864	610	605	629 598	617 585
cis-$[\mathrm{Ru(dmva)_2(NO)Br}]$	1910 1903	—1868	610	605	626 ?	615 580
cis-$[\mathrm{Ru(dmva)_3(NO)}]$	1930— 1910	1890	604	599	627 592	616 580

[a] Obscured between 585 and 630 cm^{-1}. [b] Obscured between 585 and 610 cm^{-1}.



(I)

In the 650—4 000 cm^{-1} region are found the most characteristic vibrations of the L–L ligands, $\nu(\mathrm{C^2{=}O})$, $\nu(\mathrm{C^4{=}O})$, $\nu(\mathrm{C^6{=}O^8})$, $\nu(\mathrm{C^5{=}N^7})$, and $\nu(\mathrm{N^7{-}O^9})$, which have been assigned as shown in Tables 1 and 2 by reference to data on analogous complexes.[14,15,20,22-24,40] It is noteworthy that in this region the spectra of the complexes $[\mathrm{Ru(L{-}L)_3}]^-$ do not display more bands than those of

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* During the preparation of this paper, the crystal structure was reported[39] of the salt $\mathrm{[NH_4][Fe^{II}(H_2va)_3]}{\cdot}$*ca.* $4.5\mathrm{H_2O}$ in which the anion has a similar configuration to $[\mathrm{Ru^{II}(H_2va)_3}]^-$.

[37] B. M. Graven and Y. Mascarenhas, *Acta Cryst.*, 1964, **17**, 407.

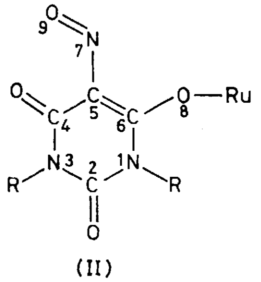
[38] H. Gillier, *Bull. Soc. chim. France*, 1965, 2373; 1975, 2385.

[39] C. L. Raston and A. H. White, *J.C.S. Dalton*, 1976, 1915 and refs. therein.

[40] M. Kimura, Y. Kuroda, H. Takagi, and M. Kubo, *Bull. Chem. Soc. Japan*, 1960, **33**, 1086; K. Burger, I. Ruff, and F. Ruff, *J. Inorg. Nuclear Chem.*, 1965, **27**, 179.

the corresponding free L–L⁻ ligands, which is in agreement with the complete equivalence of the three chelate rings demonstrated by *X*-ray diffraction.[17] In contrast, most of the above vibrations are doubled in the nitrosyl complexes $[Ru(L\text{–}L)_2(NO)X]$ (X = Cl, Br, or unidentate L–L). This is in accordance with the *cis*-Ru(NO)X configuration which makes the two chelate rings non-equivalent.

Comparison of the spectra of $[Ru(L\text{–}L)_2(NO)X]$ (X = Cl or Br) with those of $[Ru(L\text{–}L)_3(NO)]$ reveals in the latter the presence of three or four more bands in the 650—4 000 cm^{-1} region which are characteristic [25] of the unidentate L–L ligands: at 1 115, 1 152, 1 355, and 1 381 cm^{-1} for $[Ru(H_2va)_3(NO)]$; at 1 164, 1 225, and 1 470 cm^{-1} for $[Ru(dmva)_3(NO)]$. The assignments of these bands (Tables 1 and 2) are dependent [41] on the assumption that the co-ordination occurs *via* O^8 in the dominant canonical form (II). This is the most probable structure from the complete i.r. and n.m.r. studies, in accordance with the existence [41d] of the complexes $[Ru(Hba)_2(NO)Cl_3]^{2-}$ and $[Ru(Hba)_5(NO)]^{2-}$ in which the barbiturate anions (enolate Hba⁻) are also co-ordinated to ruthenium through O^8 with $\nu(C^6\text{–}O^8)$ at 1 130 cm^{-1} comparable to 1 115—1 152 cm^{-1} found in $[Ru(H_2va)_3(NO)]$.



(II)

The spectra of $[Ru(L\text{–}L)_3]^-$ in the 100—650 cm^{-1} region display several bands in addition to those observed for the corresponding free L–L⁻ ligands. These bands, which are also present in the spectra of the nitrosyl complexes, may be assigned to ruthenium–bidentate L–L ligand vibrations [42] with a major contribution of $\nu(Ru\text{–}O^8)$ at *ca.* 550—610 and 445—490 cm^{-1},[43] and of $\nu(Ru\text{–}N^7)$ at *ca.* 310—335 and 270—275 cm^{-1}.[44] As a result, the band of medium intensity at 512 cm^{-1} for $[Ru(H_2va)_3(NO)]$ and at 473 cm^{-1} for $[Ru(dmva)_3(NO)]$ can be assigned to the Ru–O^8 (unidentate L–L) stretching vibration, in accordance with similar reported values of ν(M–OR) in metal alkoxides [45] and with the structure (II).

The band of high intensity at 320 cm^{-1} in $[Ru(H_2va)_2(NO)Cl]$ and at 339 cm^{-1} in $[Ru(dmva)_2(NO)Cl]$ was identified as ν(Ru–Cl) by its shift down to 240 and 250 cm^{-1}, respectively, on substitution of chloride by bromide in the co-ordination sphere of ruthenium.

Assignments of the Ru–N–O *bands.* These have been made by using ^{15}NO (see Table 3) and by reference to data on a series of ^{14}N and ^{15}N complexes, $[Ru(NO)X_5]^{2-}$ (ref. 46) and *trans*-$[Ru(NO)(das)_2X]^{2+}$.[47] The NO stretching frequencies in our complexes are among the highest reported for ruthenium nitrosyl complexes.[7,48] This indicates the high electrophilic character [49] of the $[NO]^+$ group linearly co-ordinated to Ru^{II}, particularly in $[Ru(H_2va)_2(NO)Cl]$ where it undergoes nucleophilic attack by the barbiturate anion (Hba⁻) to afford $[Ru(H_2va)_3]^-$ with liberation of HCl.[50]

The electrophilicity of co-ordinated NO is related to the π-backbonding properties of the bidentate L–L ligands as shown by the significant shift in ν(NO) for $[Ru(L\text{–}L)_2(NO)X]$ (X = Cl or Br) from 1 950 to 1 910 cm^{-1} on substitution of the protons on N^1 and N^3 by the ' electron-releasing ' methyl groups. Indeed, this substitution causes a decrease in the π-acceptor character of the L–L ligands which leads to an increased $d_\pi(Ru)\rightarrow\pi^*(NO)$ electron transfer, weakening the N–O bond. It should be noted in this context that, in going from a complex of the type $[Ru(L\text{–}L)(NO)Cl_3]$ [51] to the corresponding $[Ru(L\text{–}L)_2(NO)Cl]$, ν(NO) always increases if L–L is a good π-acceptor ligand {for example, ν(NO) at 1 880 cm^{-1} in $[Ru(phen)(NO)Cl_3]$ [52] and 1 932 cm^{-1} in $[Ru(phen)_2(NO)Cl]^{2+}$ (ref. 7)}, and the reported ν(NO) values for complexes of the type $[Ru(L\text{–}L)_2(NO)Cl]$ reflect the increasing π-acceptor character of the L–L ligands in the order: $[S_2CNR_2]^-$ (1 803—1 830 cm^{-1}) [25] < pentane-2,4-dithionate (pdt⁻) (1 840 cm^{-1}) [53a] $\leqslant$ pd⁻ (1 884 cm^{-1}) [14] $\sim$ das (1 880—1 900 cm^{-1}) [47] < dmva⁻ (1 910 cm^{-1}) < bipy,phen (1 932 cm^{-1}) [7] < H$_2$va⁻ (1 950 cm^{-1}).

The fact that ν(NO) and ν(RuN) for $[Ru(L\text{–}L)_2(NO)X]$ (L–L = H$_2$va⁻ or dmva⁻) do not change with replacement of chloride by bromide may be related to the *cis*-Ru(NO)X configuration in these complexes, since it has been found previously that ν(NO) in *cis*-$[Ru(L\text{–}L)_2(NO)X]^{2+}$ (L–L = bipy or phen) [7] and in *cis*-$[Mo\{HB(C_3HMe_2N_2)_3\}(NO)X_2]$ [53b] is also insensitive to X = Cl

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[41] (*a*) B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321; (*b*) K. Nakanishi, ' Infrared Absorption Spectroscopy,' Holden-Day, San Francisco, 1964, p. 38; (*c*) T. Ishiyama, *Bull. Chem. Soc. Japan*, 1975, **48**, 443; (*d*) S. Sueur, C. Bremard, and G. Nowogrocki, *Bull. Soc. chim. France*, 1976, 1051.

[42] A. Bigotto, V. Galasso, and G. Dealti, *Spectrochim. Acta*, 1972, **A28**, 1581.

[43] S. Pinchas and J. Shamir, *J.C.S. Perkin II*, 1975, 1098 and refs. therein.

[44] (*a*) D. M. Adams, ' Metal–Ligand and Related Vibrations,' Edward Arnold, London, 1967, p. 284; (*b*) J. Dehand and J. Jordanov, *Inorg. Chim. Acta*, 1976, **17**, 37 and refs. therein.

[45] Ref. 44(*a*), p. 241.

[46] E. Miki, *Bull. Chem. Soc. Japan*, 1968, **41**, 1835.

[47] M. S. Quinby and R. D. Feltham, *Inorg. Chem.*, 1972, **11**, 2468.

[48] Ref. 44(*a*), p. 292; W. P. Griffith, J. Lewis, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 38; P. Gans, *Chem. Comm.*, 1965, 144.

[49] J. H. Swinehart, *Co-ordination Chem. Rev.*, 1967, **2**, 385; F. Bottomley, W. V. Brooks, S. G. Clarkson, and S. B. Tong, *J.C.S. Chem. Comm.*, 1973, 919.

[50] S. Sueur, C. Bremard, and G. Nowogrocki, unpublished work.

[51] M. B. Fairey and R. J. Irving, *J. Chem. Soc.* (*A*), 1966, 475.

[52] J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, **7**, 32.

[53] (*a*) G. A. Heath and R. L. Martin, *Austral. J. Chem.*, 1970, **23**, 2297; (*b*) J. A. McCleverty, D. Seddon, N. A. Bailey, and N. W. J. Walker, *J.C.S. Dalton*, 1976, 898.

or Br, whereas the replacement of Cl by Br or I in *trans*-$[Ru(NO)(NH_3)_4Cl]^{2+}$ (ref. 54) and in *trans*-$[Ru(NO)(das)_2Cl]^{2+}$ (ref. 47) leads to a significant decrease in the ν(NO) and ν(RuN) frequencies, due to the increase in the *trans*-directing influence of X in the order Cl < Br < I.

The replacement of Cl or Br in *cis*-$[Ru(H_2va)_2(NO)X]$ by unidentate H_2va leads to a decrease in ν(NO) (1 950 to 1 924 cm^{-1}) and an increase in ν(RuN) (620 to 641 cm^{-1}), due to the increase in electron density at Ru by co-ordination *via* O^8. In *cis*-$[Ru(dmva)_3(NO)]$ this effect is overcome by the greater steric interactions between the ligands, leading to inverse shifts in ν(NO) (1 910 to 1 930 cm^{-1}) and ν(RuN) (610 to 604 cm^{-1}) on substitution of Cl or Br by unidentate dmva.

TABLE 4

Hydrogen-1 n.m.r. spectra (chemical shifts in p.p.m. downfield from $SiMe_4$)

(*a*) Values of δ(N–H) [a] for the violurato-complexes

Complex			
$Na[H_2va]$		10.10 (vbr) (N^3–H + N^1–H)	
$Na[Ru(H_2va)_3]$		10.70 (N^3–H)	11.93 (br) (N^1–H)
cis-$[Ru(H_2va)_2(NO)Cl]$		11.55	11.68 (two N^3–H)
cis-$[Ru(H_2va)_2(NO)Br]$		11.57	11.70 (two N^3–H)
cis-$[Ru(H_2va)_3(NO)]$	two bidentate H_2va:	11.45	11.65 (two N^3–H)
	+		
	one unidentate H_2va:	10.92—11.00 (N^3–H + N^1–H) (1.2 : 0.8) [b]	

All the peaks for a given complex are of equal integration, unless otherwise stated (see *b*). [b] Integration ratio.

(*b*) Values of $\delta(N–CH_3)$ [a] for the 1,3-dimethylviolurato-complexes

Complex					
Na[dmva]		3.06 (N^3–Me)		3.28 (N^1–Me)	
$Na[Ru(dmva)_3]$		3.10 (N^3–Me)		3.33 (N^1–Me)	
cis-$[Ru(dmva)_2(NO)Cl]$		3.12	3.18 (two N^3–Me)	3.35	3.50 (two N^1–Me)
cis-$[Ru(dmva)_2(NO)Br]$		3.14	3.20 (two N^3–Me)	3.36	3.51 (two N^1–Me)
cis-$[Ru(dmva)_3(NO)]$	two bidentate dmva:	3.13	3.20 (two N^3–Me)	3.36	3.51 (two N^1–Me)
	+				
	one unidentate dmva:	3.10 (one N^3–Me)		3.42 (one N^1–Me)	

Hydrogen-1 *n.m.r. spectra*. The ^1H n.m.r. spectra of all the complexes were recorded in $(CD_3)_2SO$. They are summarized and compared in Table 4.

The spectrum of Na[dmva] displays two distinct methyl resonances of equal intensity, due to the non-equivalence of $N^1–CH_3$ and $N^3–CH_3$ in the unco-ordinated $dmva^-$ anion. In contrast, the spectrum of $Na[H_2va]$ exhibits only one very broad signal at a much lower field, due to the rapid exchange of the two protons between the non-equivalent N^1 and N^3 sites of the free H_2va^- anion. This signal splits into two peaks of equal integration at even lower fields, on bidentate co-ordination of H_2va^- in $[Ru(H_2va)_3]^-$. By analogy with the n.m.r. spectra of other ketone oximato and related complexes,[20a,23] the broad peak at lowest field is assigned to the N^1–H proton, and the sharp signal at highest field to the N^3–H proton [structure (I)]. A similar situation occurs in $[Ru(dmva)_3]^-$, except that in this case the downfield shifts of the $N^1–CH_3$ and $N^2–CH_3$ signals on bidentate co-ordination of $dmva^-$ are relatively smaller. The fact that the n.m.r. spectra of $[Ru(L–L)_3]^-$ display only two signals reveals that the complexes exist only in the *cis–cis* (C_3) form in $(CD_3)_2SO$ solution, as in the solid state.[17]

In going from $[Ru(dmva)_3]^-$ to *cis*-$[Ru(dmva)_2(NO)X]$ (X = Cl or Br), the $N^1–CH_3$ and $N^3–CH_3$ signals are both shifted downfield and split into two peaks of equal integration, in accordance with the *cis* arrangement of the halide and the nitrosyl around ruthenium. In the corresponding *cis*-$[Ru(H_2va)_2(NO)X]$ complexes, the

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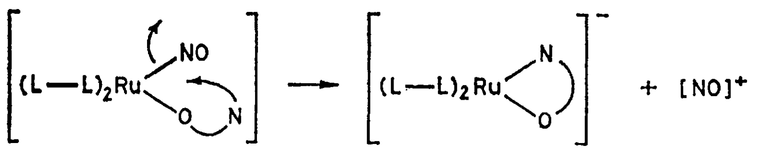
[54] E. E. Mercer, W. A. McAllister, and J. R. Durig, *Inorg. Chem.*, 1966, **5**, 1881.

labilizing effect of NO and X on the N^1–H protons is so strong that they exchange with deuterium too rapidly to be detected on the n.m.r. time scale, whereas the weaker deshielding effect on the two non-equivalent N^3–H protons allows them to resonate at two distinct chemical shifts.

The continuous deshielding of the protons, in going from unco-ordinated L–L to $[Ru(L–L)_3]^-$ and to *cis*-$[Ru(L–L)_2(NO)X]$, can be related to the corresponding decrease in their pK_a values which we have measured [32] by potentiometry for the violurato-complexes. We found that: (*i*) the electrostatic effect of bidentate co-ordination of the H_2va^- ligands to the positively charged ruthenium(II) centre makes the N^1 atoms in $[Ru(H_2va)_3]^-$ less basic than in the free ligand, whereas the strong basicity of the N^3 atoms is only very little affected; (*ii*) the co-ordination of the nitrosyl and the halide to the bisvioluratoruthenium(II) centre makes the N^1–H protons in *cis*-$[Ru(H_2va)_2(NO)X]$ even more acidic ($pK_a \simeq 3$) and the N^3 atoms less basic ($pK_a \simeq 9.5$) than in $[Ru(H_2va)_3]^-$, which can be explained [34] by the decrease in back donation, $t_{2g}(Ru) \rightarrow \pi^*$(bidentate H_2va), resulting from the competitive electron transfer $d_\pi(Ru) \rightarrow \pi^*(NO)$.



N.m.r. Study of the Dissociation: cis-$[Ru(L–L)_3(NO)] \longrightarrow [Ru(L–L)_3]^- + [NO]^+$.—The n.m.r. spectrum of *cis*-$[Ru(dmva)_3(NO)]$ recorded *ca.* 10 min after its dissolution in $(CD_3)_2SO$ exhibits six signals of equal integration, in accordance with the *cis* arrangement of the nitrosyl and the unidentate dmva around ruthenium. The four signals which are related to those of *cis*-$[Ru(dmva)_2(NO)X]$ (X = Cl or Br) are assigned to the methyl groups of the two bidentate dmva, the two remaining peaks being attributed to the methyl groups of unidentate dmva. The relatively great difference observed between the latter (3.10 p.p.m. for N^3–CH_3 and 3.42 p.p.m. for N^1–CH_3) is to be expected if the co-ordination of unidentate dmva occurs *via* O^8 [structure (II)].

After *ca.* 20 min the spectrum begins to change, even when the solution is kept in darkness: the signals characteristic of *cis*-$[Ru(dmva)_3(NO)]$ diminish in intensity, whilst the two peaks at 3.10 and 3.33 p.p.m., characteristic of $[Ru(dmva)_3]^-$, increase in intensity. This confirms the dissociation *cis*-$[Ru(dmva)_3(NO)] \longrightarrow [Ru(dmva)_3]^- + [NO]^+$ which has already been observed in acetonitrile solution from the electronic spectra. The transformation is almost complete after *ca.* 2 h.

The complex *cis*-$[Ru(H_2va)_3(NO)]$ undergoes the same transformation, but more rapidly. Indeed, *ca.* 10 min after its dissolution in $(CD_3)_2SO$ its n.m.r. spectrum exhibits the signals of $[Ru(H_2va)_3]^-$ at 10.70 and 11.93 p.p.m., in addition to four peaks of *cis*-$[Ru(H_2va)_3(NO)]$ at 11.45 (intensity 1.0) and 11.65 (1.0) p.p.m. and at 10.92 (1.2) and 11.00 (0.8) p.p.m., due to the N^3–H protons of the two bidentate H_2va and to the N^3–H and N^1–H protons of unidentate H_2va, respectively. The small difference observed between the last two chemical shifts indicates that unidentate H_2va co-ordinates to ruthenium *via* N^7 rather than O^8. However, a fast dynamic process at room temperature, in which the O^8 and O^4 atoms co-ordinate to ruthenium, may also account for the 'similarity' of the two protons of unidentate H_2va. In order to verify this hypothesis and to slow down the dissociation of *cis*-$[Ru(H_2va)_3(NO)]$, we tried to record its spectrum at low temperatures in other solvents than $(CD_3)_2SO$, the melting point of the latter (18 °C) precluding its use. Unfortunately, the solubility of the violurato-complex is either too low in the solvents used ($CDCl_3$, CD_2Cl_2, CD_3Cl, CCl_4, *etc.*) or the protons exchanged with deuterium (in the case of D_2O, CD_3OD, C_2D_5OD, *etc.*).

The transformation *cis*-$[Ru(H_2va)_3(NO)] \longrightarrow [Ru(H_2va)_3]^- + [NO]^+$ in $(CD_3)_2SO$ is almost complete after 1 h, the n.m.r. spectrum showing only very weak peaks of *cis*-$[Ru(H_2va)_3(NO)]$ or of decomposition products, in addition to the sharp signals of $[Ru(H_2va)_3]^-$ at 10.70 and 11.93 p.p.m. It is interesting to note that the latter signal appeared only as a broad peak in the spectrum of $Na[Ru(H_2va)_3]$.

The kinetics of the dissociation have been studied [26] spectrophotochemically in water where the mechanism appears to be an 'acid-catalyzed denitrosylation.' Such a mechanism is not possible in the aprotic solvents MeCN and dmso. We have also seen that the dissociation is not a photochemical process. The fact that the complexes *cis*-$[Ru(L–L)_2(NO)X]$ (X = Cl or Br) do *not* release $[NO]^+$ under the same conditions provides good support for the assertion that the transformation *cis*-$[Ru(L–L)_3(NO)] \longrightarrow [Ru(L–L)_3]^- + [NO]^+$ is essentially due to the strong 'chelate effect' of the L–L ligands which leads to the closure of the chelate ring and concomitant displacement of the nitrosyl. As far as we know, this is the first reported example of such an intramolecular transformation in the chemistry of transition-metal nitrosyl complexes, the inertness of the MNO group to cleavage of the M–N bond being the most commonly observed feature.[2,4,8,9] However, it is known [18] that a few nitrosyl complexes {*e.g.* $[Co(NO)(dmg)_2]$ [dmg = dimethylglyoximate(2−)]} can transfer NO to other transition-metal complexes.[55] Although we do not know in which form the nitrosyl group is

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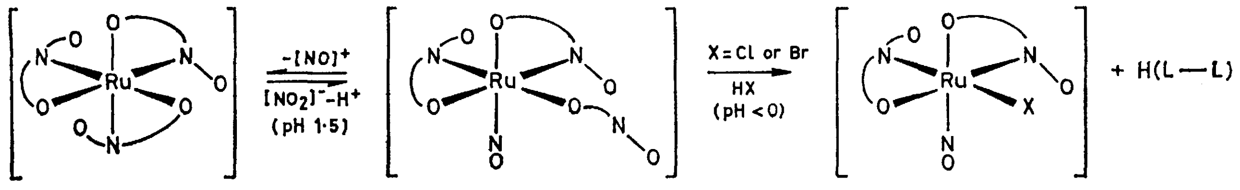
[55] C. B. Ungermann and K. G. Caulton, *J. Amer. Chem. Soc.*, 1976, **98**, 3862.

released in our case ([NO]$^+$?), it is probably in an ' activated ' form. It is therefore of interest to test the complexes *cis*-[Ru(L–L)$_3$(NO)] as ' clean ' nitrosylating agents in polar aprotic organic solvents; such studies are in progress.

Conclusion.—On the basis of the results of this work, the most probable structures of the different complexes studied and their inter-relations are as follows:



fac-[Ru(L—L)$_3$]$^-$ *cis*-[Ru(L—L)$_3$(NO)] *cis*-[Ru(L—L)$_2$(NO)X]

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