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Preparation and Properties of some Ruthenium(II) Complexes with Violurate Ligands

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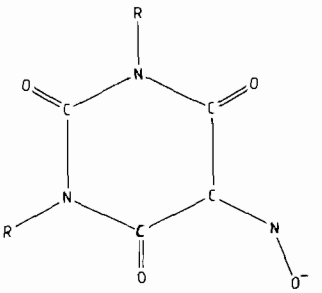
Complexes with the general formuale, $[Ru(VR_2)_3]^-$, $[Ru(VR_2)_2Cl_2]^{2-}$, $[Ru(VR_2)_2XNO]$ and $[Ru(VR_2)_2YNO]ClO_4$ {where VR_2 = violurate; R = H or CH_3; X = Cl^-, NO_3^- or OH^-, Y = CH_3CN, $(CH_3)_2SO$, C_5H_5N, $C_3H_4N_2$, or H_2O}, have been synthesized by new and improved methods. Some properties of these compounds are also reported.

Introduction

The intriguing diversity of the chemistry displayed by metal bound nitric oxide complexes has inspired extensive examination of their synthesis [1] and properties [2–8]. The prevailing view arising from these studies is that the range of behaviour of the M–NO group may be rationalized by a variation in the effective charge on the NO from NO^- to NO^+. Recently, the chemical reactivity of the nitrosyl complexes has been examined more thoroughly, particularly in relation to the more readily measured spectroscopic properties [9]. The chemical properties of such complexes are also manifest in their pharmacological behaviour. Reports of inhibition of DNA synthesis, anticancer activity [10], and of hypotensive action [11, 12] have all appeared in the literature.

Our efforts, including those published in this paper, have been directed to extending the range of M–NO complexes that are available for study, particularly complexes with high NO^+ character, because of their potential biological activity. We report here on the preparation and properties of some ruthenium(II) complexes incorporating the unusual violurate ligands(I). Complexes of this type, which were first reported by Bremard *et al.* [13–17], appeared to be good prospects for biological studies, though so far they have proved disappointing. Ten compounds with the general formula $[Ru(VR_2)_2(X)NO]$ (R = H or CH_3) have been isolated and characterised along with their synthetic precursors. Alternative, simpler, methods have been found for compounds that were previously reported. For example a more direct route to the formation of $[Ru(VR_2)_3]^-$ has been established. The synthesis and properties of $[Ru(VR_2)_2Cl_2]^-$ complexes are reported for the first time.



VIOLURATE, VR_2^-

Results

Synthesis

Bremard *et al.* [15] prepared the tris violurate complexes, $[Ru(VR_2)_3]^-$, by an interesting route from $[Ru(NO_2)_4(NO)OH]$ and barbituric acid. However they can be prepared more simply by refluxing either $RuCl_3 \cdot XH_2O$ with $H \cdot VR_2$ in ethanol or $K_2[RuCl_5(H_2O)]$ with $Na \cdot VR_2$ in aqueous solutions. Exclusion of oxygen and light is not necessary in these preparations. The bis complexes, $[Ru(VR_2)_2Cl_2]^{2-}$, which have not been reported previously, can then be prepared easily by heating solutions of $[Ru(VR_2)_3]^-$ in dilute aqueous HCl.

The tris violurate complexes were used by Bremard, Muller, Nowogrocki and Sueur [15, 16] to prepare $[Ru(VR_2)_2(Cl)NO]$. These complexes and $[Ru(V(CH_3)_2)_2(NO_3)NO]$ can also be prepared conveniently by reactions of $[Ru(NO_2)_4(OH)NO]^{2-}$ with the corresponding $H \cdot VR_2/Na \cdot VR_2$ in the presence of an appropriate acid, such as HCl for the formation of the chloro complex. The addition of some acid appears to be necessary, particularly if $Na \cdot VR_2$ is used. In each case, the reaction was accompanied by evolution of brown fumes (oxides of nitrogen). This observation combined with the

need for a moderately strong acid suggests that the reaction involves the acid catalysed hydrolysis of the coordinated NO_2^- groups [18], followed by substitution of the resulting aquo nitrosyl complex by available ligands. In general, complexes of the type $[Ru(VR_2)(Y)NO]$ are formed in the presence of VR_2^-, where Y is the conjugate base of the acid used.

The complexes $[Ru(VR_2)_2(Cl)NO]$, can also be prepared from $[Ru(VR_2)_2Cl_2]^{2-}$ by the nitrosylation reaction (attack of NO^+ on the metal complex), as described for the synthesis of $[Ru(L-L)_2(Cl)NO]^{2+}$ {where (L–L) is either 2,2′-bipyridine or 1,10-phenanthroline} [19].

Complexes of the types $[Ru(V(CH_3)_2)_2(X)NO]$ and $[Ru(V(CH_3)_2)_2(Y)NO]ClO_4$ {where X = Cl^- or OH^-, Y = H_2O, $(CH_3)_2SO$, pyridine or imidazole} were prepared by substituting the labile coordinated CH_3CN group of $[Ru(V(CH_3)_2)_2(CH_3CN)NO]^+$ with the appropriate ligand.

i.e.

$$[Ru(V(CH_3)_2)_2(CH_3CN)NO]^+ \xrightarrow[CH_3CN]{\text{dil.HCl}} [Ru(V(CH_3)_2)_2(Cl)NO]$$

$$[Ru(V(CH_3)_2)_2(CH_3CN)NO]^+ \xrightarrow[H_2O]{} [Ru(V(CH_3)_2)_2(OH)NO] \xrightarrow{\text{dil. } HClO_4} [Ru(V(CH_3)_2)_2(H_2O)NO]ClO_4$$

$$[Ru(V(CH_3)_2)_2(CH_3CN)NO]^+ \xrightarrow[CH_3CN]{Y} [Ru(V(CH_3)_2)_2(Y)NO]^+$$

where Y = $(CH_3)_2SO$, C_5H_5N or $C_3H_4N_2$.

$[Ru(V(CH_3)_2)_2(CH_3CN)NO]ClO_4$ is easily prepared by refluxing $[Ru(V(CH_3)_2)_2(NO_3)NO]$ in CH_3CN with a small volume of $HClO_4$.

Structure and Formulation of the Complexes

$[Ru(VR_2)_3^-]$

The pmr spectra of $Na{\cdot}VH_2$ and $Na{\cdot}V(CH_3)_2$ show two distinct peaks of equal intensity assignable to the non-equivalent N^1-R and N^3-R protons (Fig. 1). The peaks at lowest field and highest field have previously been assigned [15] to the N^1-R and N^3-R protons respectively, and they are shifted to lower field on coordination consistent with the known geometry of these complexes [13]. The tris violurato complexes, $[Ru(VH_2)_3]^-$ and $[Fe(VH_2)_3]^-$ have been shown to adopt a *fac* geometry in which the ligand binds through one carbonyl oxygen (O^9) and the oxime nitrogen (N^7) external to the ring [13, 19, 20].

$[Ru(VR_2)_2Cl_2]^{2-}$

There is no direct information on the stereochemistry of $[Ru(VR_2)_2Cl_2]^{2-}$ complexes; both *cis* and *trans* configurations are consistent with their pmr spectra. However the *cis* configuration is favoured because of their ready conversion to *cis* nitrosyl complexes and their preparation from $[Ru(VR_2)_3]^-$. In view of the asymmetry of the VR_2^- ligands, *i.e.* non-equivalent N^1-R and N^3-R sites, five geometric isomers are possible and they can be grouped into three types: (I) *trans* chlorides with *cis* or *trans* arrangement of the VR_2^- ligands; (II) *cis* chlorides with a symmetrical disposition of the VR_2^- ligands; (III) *cis* chlorides with an unsymmetrical arrangement of the VR_2^- ligands. The pmr spectra of isomers of types (I) and (II) should show two peaks of equal intensity, while four peaks of equal intensity are expected for the isomer of type (III). As there are only two distinct methyl resonances of equal intensiy in the pmr spectrum of $[Ru(V(CH_3)_2)_2Cl_2]^2$ (Table I), it may be inferred that the isomer of type (III) is not favoured. On the other hand, the asymmetry of type (III) might be too small to be detected by pmr. This isomer is expected if the configuration of *fac.* $[Ru(VR_2)_3]^-$ was retained in the preparation of *cis*-$[Ru(VR_2)_2Cl_2]^{2-}$.

$[Ru(V(CH_3)_2)_2(Y)NO]$

The nitrosyl complexes, $[Ru(V(CH_3)_2)_2(Cl)NO]$ and complexes of the type $[Ru(V(CH_3)_2)_2(Y)NO]ClO_4$ {where Y = H_2O, CH_3CN, $(CH_3)_2SO$, C_5H_5N or $C_3H_4N_2$} are best represented as six coordinate, *cis* complexes, based on their analytical data and spectroscopic properties. Most significantly, the pmr spectra (Table I) of these nitrosyl complexes exhibit four peaks of equal intensity attributable to the methyl protons of the chelated dimethylviolurate groups, which is consistent with *cis* but not *trans* configurations. It should be noted that complexes with coordinated NO_3^-, $(CH_3)_2SO$, H_2O or CH_3CN do not give rise to simple four-line pmr spectra in all solvents, but this behaviour can be attributed to the substitution of the labile coordinated groups by solvent molecules (to be discussed below).

$[Ru(VH_2)_2(Cl)NO]$

By analogy, $[Ru(VH_2)_2(Cl)NO]$ is also expected to be a six coordinate, *cis* complex, though its pmr spectrum displays only two peaks of equal intensity instead of four peaks. The two peaks have been assigned to the two non-equivalent N^3-H protons [15], while the absence of the N^1-H signals may be attributed to a rapid exchange of the acidic N^1-H

TABLE I. Proton Magnetic Resonance Spectra.

Compound	PMR Spectra (ppm)	
	$(CD_3)_2SO$	CD_3CN
$H{\cdot}VH_2$	11.42	
$H{\cdot}V(CH_3)_2$	3.19, 3.13	
$Na{\cdot}VH_2$	10.33, 9.94	
$Na{\cdot}V(CH_3)_2$	3.28, 3.06	
$K[Ru(VH_2)_3]$	11.93, 10.69	
$K[Ru(V(CH_3)_2)_3]$	3.37, 3.12	
$Ba[Ru(VH_2)_2Cl_2]$	11.42, 10.18	
$K_2[Ru(V(CH_3)_2)_2Cl_2]$	3.46, 3.12	
$[Ru(VH_2)_2(Cl)NO]$	11.73, 11.58[a]	
$[Ru(V(CH_3)_2)_2(Cl)NO]$	3.49, 3.33, 3.18, 3.11	3.55, 3.36, 3.25, 3.17
$[Ru(V(CH_3)_2)_2(OH)NO]$	3.45, 3.17	3.51, 3.23
$[Ru(V(CH_3)_2)_2(NO_3)NO]$	3.50, 3.38, 3.12, 3.09	3.57, 3.41, 3.23, 3.18
	3.42, 3.18	3.48, 3.44, 3.23, 3.16
$[Ru(V(CH_3)_2)_2(H_2O)NO]HSO_4$	3.54, 3.39, 3.20, 3.15	
	3.52, 3.23	
$[Ru(V(CH_3)_2)_2(H_2O)NO]ClO_4$	3.54, 3.39, 3.20, 3.15	3.57, 3.41, 3.26, 3.23
	3.52, 3.23	3.63, 3.33, 3.27, 3.19
$[Ru(V(CH_3)_2)_2(CH_3CN)NO]ClO_4$	3.54, 3.39, 3.20, 3.15	3.57, 3.41, 3.26, 3.23
	3.52, 3.23	
$[Ru(V(CH_3)_2)_2((CH_3)_2SO)NO]ClO_4$	3.54, 3.38, 3.21, 3.15	3.57, 3.41, 3.26, 3.23
	3.52, 3.23	3.50, 3.35, 3.16, 3.15
$[Ru(V(CH_3)_2)_2(C_5H_5N)NO]ClO_4$	3.58, 3.31, 3.22, 3.10	3.64, 3.33, 3.28, 3.16
	3.55, 3.31, 3.21, 3.15	3.63, 3.30, 3.28, 3.18

[a] N^1-H signals are not observed.

proton ($pk_a \cong 3$) [14] in the presence of a trace of H_2O in $(CD_3)_2SO$.

[Ru(V(CH$_3$)$_2$)$_2$(OH)NO]

The hydroxo complex appears to be 'normal' in all respects except for its pmr spectrum. The appearance of characteristic Ru-OH absorption bands (3460, 3527, 3585 cm^{-1}) in its infra-red spectrum and a peak at 7.23 ppm (which is not observed on addition of D_2O) assignable to an OH proton in its pmr spectrum, strongly support the formulation of the complex. However, the pmr spectrum of the complex displays only two distinct methyl resonances of equal intensity. All the other nitrosyl complexes exhibit four methyl resonances. Indeed the four lines characteristic of *cis*-$[Ru(V(CH_3)_2)_2(Cl)NO]$ are observed on addition of DCl to $[Ru(V(CH_3)_2(OH)NO]$ solutions. Three explanations may be proposed in an attempt to rationalise these observations.

(1) The complex, $[Ru(V(CH_3)_2)_2(OH)NO]$ may prefer a *trans* rather than a *cis* configuration. A corollary of this hypothesis is, of course, that *trans*-$[Ru(V(CH_3)_2)_2(OH)NO]$ should undergo a change in configuration when it is prepared from and converted to other *cis* complexes.

(2) The coordinated NO^+ and OH^- groups are rapidly interchanging their positions in a *cis* complex. Speculative pathways involving intramolecular interaction of the OH^- nucleophile with the NO^+ electrophile may be envisioned, as for example:

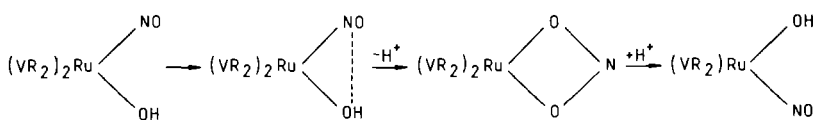


TABLE II. Nitrosyl Stretching Frequencies (ν_{NO}).

Compound	ν_{NO} (cm^{-1})	
	Nujol mull	$(CH_3)_2SO$
$[Ru(VH_2)_2(Cl)NO]$	1947	1915
$[Ru(V(CH_3)_2)_2(Cl)NO]$	1910	1900
$[Ru(V(CH_3)_2)_2(OH)NO]$	1895	1845
$[Ru(V(CH_3)_2)_2(NO_3)NO$	1920	1910
$[Ru(V(CH_3)_2)_2(H_2O)NO]HSO_4$	1944	1910
$[Ru(V(CH_3)_2)_2(H_2O)NO]ClO_4$	1925	1910
$[Ru(V(CH_3)_2)_2(CH_3CN)NO]ClO_4$	1940	1910
$[Ru(V(CH_3)_2)_2((CH_3)_2SO)NO]ClO_4$	1920	1910
$[Ru(V(CH_3)_2)_2(C_5H_5N)NO]ClO_4$	1929	1915
$[Ru(V(CH_3)_2)_2(C_3H_4N_2)NO]ClO_4$	1922	1915

Such species have previously been proposed as intermediates in the substitution-induced nitro–nitrito isomerisation [21]. An attempt has been made to observe the rate of intramolecular exchange at low temperatures in CD_3CN but the pmr spectrum of $[Ru(V(CH_3)_2)_2(OH)NO]$ in this mechanism is essentially unchanged within the temperature range of 323 K to 230 K.

(3) The compound has the *cis* configuration but the two line spectrum results from the fortuitous coincidence of the chemical shifts of the methyl protons. This possibility appears unlikely since the ^{13}C nmr spectrum also has only two lines (of equal intensity) attributable to the methyl carbons. (Full spectrum 174.3, 151.5, 148.8, 138.8, *29.7, 27.6* ppm).

The second of these hypotheses is preferred mainly because there seems no plausible chemical reason for the hydroxy complex to be the only complex that prefers the *trans* complex.

[Ru(V(CH$_3$)$_2$)$_2$(NO$_3$)NO]

The pmr spectrum of this complex shows more lines than expected from this formula. Some of these can be assigned if it is assumed that the coordinated NO_3^- group is labile and can be substituted by a solvent molecule. This conclusion is supported by the observation that the addition of a small volume of conc. DCl converts the complex spectrum into a four line spectrum assignable to *cis*-$[Ru(V(CH_3)_2)_2(Cl)NO]$. The 'brown ring' test gives a positive result with the complex indicating the presence of nitrate. However, its infra-red spectrum is virtually identical to that of $[Ru(V(CH_3)_2)_2(Cl)NO]$ when measured using nujol mulls (NaCl or AgCl plates) or KBr discs, except in the region around 1900 cm^{-1}. Nevertheless, in view of the analytical data and the apparent lability of a coordinated group, the complex is probably best represented by the formula $[Ru(V(CH_3)_2)_2(NO_3)NO]$.

[Ru(V(CH$_3$)$_2$)$_2$(H$_2$O)NO]·HSO$_4$

In the solid state this complex may have bisulfate coordinated rather than water. The infra-red spectrum of the complex shows the presence of bisulfate group [22], but coordinated and uncoordinated bisulfate group cannot be distinguished by this method.

Infra-red Spectra

The infra-red spectra of all the complexes being examined show characteristic absorption bands of the coordinated violurate and dimethylviolurate groups [3], while an additional intense NO absorption band around 1900 cm^{-1} is observed for all the nitrosyl complexes (Table II). The high ν_{NO} values of these nitrosyl complexes suggests that the coordinated NO groups have considerable positive charge and electrophilic character [9], and thus are expected to be susceptible to attack by nucleophiles. Solution-infrared spectra in dimethylsulphonide exhibit relatively low ν_{NO} frequencies (Table II). This observation is probably a consequence of an interaction of the nucleophilic solvent with the electrophilic NO. The sequence and span of the ν_{NO} frequencies in the violurate complexes are remarkably similar to the equivalent bipyridyl complexes [23] ($[Ru(bpy)_2(X)NO]$).

Ultraviolet–Visible Spectra

Ultraviolet–visible absorption spectra of the complexes are recorded in Table III.

$[Ru(VR_2)_3]^-$ and $[Ru(VR_2)_2Cl_2]^{2-}$ spectra are dominated by the presence of an intense charge transfer band ($t_{2g} \rightarrow \pi^*$) in the visible region. The shift to longer wavelengths in the chloro complex probably

TABLE III. Ultraviolet–Visible Spectra.

Compound	Wavelength at Maximum (nm) [Molar Extinction Coefficient (mol^{-1} dm^3 cm^{-1})]		
$NaVH_2$[a]	552 [5.3 × 10]		312 [1.2 × 10^4]
$NaV(CH_3)_2$[a]	545 [5.8 × 10]		314 [1.6 × 10^4]
$K[Ru(VH_2)_3]$[a]	495 [2.2 × 10^4]		303 [2.3 × 10^4]
$K[Ru(V(CH_3)_2)_3]$[a]	495 [2.2 × 10^4]		303 [2.6 × 10^4]
$Ba[Ru(VH_2)_2Cl_2]$[b]	573 [2.1 × 10^4]	340 sh [8.1 × 10^3]	300 [1.6 × 10^4]
$K_2[Ru(V(CH_3)_2)_2Cl]$[b]	573 [2.1 × 10^4]	340 sh [6.9 × 10^3]	298 [1.5 × 10^4]
$[Ru(VH_2)_2(Cl)NO]$[a]		377 sh [1.5 × 10^4]	322 [2.5 × 10^4]
$[Ru(V(CH_3)_2)_2(Cl)NO]$[c]	460 br [6.2 × 10^2]	380 sh [9.3 × 10^3]	326 [2.1 × 10^4]
$[Ru(V(CH_3)_2)_2(OH)NO]$[c]		363 sh [1.0 × 10^4]	324 [1.4 × 10^4]
$[Ru(V(CH_3)_2)_2(NO_3)NO]$[c]	465 br [1.2 × 10^3]	369 sh [1.9 × 10^4]	320 [1.9 × 10^4]
$[Ru(V(CH_3)_2)_2(H_2O)NO]HSO_4$[d]		377 sh [1.0 × 10^4]	325 [2.2 × 10^4]
$[Ru(V(CH_3)_2)_2(H_2O)NO]ClO_4$[c]		361 sh [1.3 × 10^4]	325 [1.8 × 10^4]
$[Ru(V(CH_3)_2)_2(CH_3CN)NO]ClO_4$[c]	465 sh [9.6 × 10^2]	357 sh [1.5 × 10^4]	324 [1.9 × 10^4]
$[Ru(V(CH_3)_2)_2((CH_3)_2SO)NO]ClO_4$[c]	417 br [2.2 × 10^3]	364 sh [1.1 × 10^4]	323 [1.6 × 10^4]
$[Ru(V(CH_3)_2)_2(C_5H_5N)NO]ClO_4$[c]	450 sh [2.1 × 10^3]	356 sh [1.4 × 10^4]	320 [1.9 × 10^4]
$[Ru(V(CH_3)_2)_2(C_3H_4N_2)NO]ClO_4$[c]	455 sh [1.5 × 10^3]	365 sh [1.3 × 10^4]	314 [1.9 × 10^4]

[a]Phosphate pH = 7 buffer. [b]10^{-3} *M* HCl. [c]CH_3CN. [d]10^{-3} *M* H_2SO_4; sh: shoulder, br: broad.

reflects an increase in the energy of the t_{2g} level through the combined effects of smaller ligand field strength and weaker π effects of chloride compared to violurate. Another absorption band around 310 nm is found in all the complexes as well as in the free ligand and is therefore assigned to an intra-ligand transition.

The absorption bands of the nitrosyl complexes are more complex. They have been discussed by Bremard *et al.* [15].

Solution Properties

The complexes $M[Ru(VR_2)_3]$, $M_2[Ru(VR_2)_2Cl_2]$ where M = Na or K and $Ba[Ru(VH_2)_2Cl_2]$ are all soluble and stable in water and in other polar solvents.

Addition of a stoichiometric amount of Ce(IV) to a solution of $[Ru(V(CH_3)_2)_3]^-$ reduces the intensity of its visible absorption spectrum by less than 10%. (A tenfold excess completely decolourizes the solutions.) This observation implies that either the Ru(III)/Ru(II) redox potential is higher than the Ce(IV)/Ce(III) redox potential (~1.5 volt) or that the Ru(III) complex is rapidly reduced to the Ru(II) complex by the solvent. No oxidation wave is observed by cyclic voltammetry below solvent decomposition (1.6 volt). Solutions of Fe(III) tris violurate also spontaneously reduce to the corresponding Fe(II) compound at pH 5 and above.

All the nitrosyl complexes, except $[Ru(V(CH_3)_2)_2(H_2O)NO]HSO_4$, are very insoluble in water though they are moderately soluble in acetonitrile and dimethylformamide and very soluble in dimethylsulphoxide. $[Ru(VH_2)_2ClNO]$ dissolves in water when sufficient base is added to deprotonate the violurate. On the other hand $[Ru(V(CH_3)_2)_2(Y)NO]$, where $Y = OH^-$ or NO_3^-, dissolve in dilute aqueous sulfuric acid (pH < 1). It appears that the

neutral hydroxy complex is converted to the cationic aqua complex by acid. On raising the pH of these solutions to between 4 and 5 a yellow precipitate of the hydroxy complex slowly forms. At higher pH the complex undergoes a complete rearrangement to give $[Ru(VR_2)_3]^-$ (and other unidentified products). These remarks also apply to $[Ru(V(CH_3)_2)_2(H_2O)NO]HSO_4$ and the nitrato complex since they all give apparently identical solutions in dilute sulfuric acid. (From pmr, solution ir and visible spectra.)

Some of the complicated behaviour in water is dependent on the lability of the unidentate ligand Y. This lability is also observed in non-aqueous solvents. Addition of HCl to solutions of $[Ru((CH_3)_2V)_2(Y)NO]$, where Y is H_2O, OH^-, $(CH_3)_2SO$, CH_3CN or NO_3, rapidly converts them to the chloro complex, as shown by pmr spectra. It is also clear from the pmr spectra that the pmr solvent replaces the ligand Y in some instances. For example, the pmr spectrum of solutions of the $[Ru(V(CH_3)_2)_2(CH_3CN)NO]$ in CD_3CN shows no evidence of coordinated CH_3CN and has lines in common with the spectra of the H_2O and $(CH_3)_2SO$ complexes in the same solvent. All these spectra may be consistently interpreted by the equilibrium.

$$[Ru(V(CH_3)_2)_2(Y)NO]^+ + CD_3CN \rightleftharpoons [Ru(V(CH_3)_2)_2(CD_3CN)NO]^+ + Y$$

In $(CD_3)_2SO$ these labile complexes all give essentially identical pmr spectra consisting of four strong lines of equal area and two weak lines. The four strong lines may be assigned to the dimethylsulphoxide complex $[Ru(V(CH_3)_2)_2((CH_3)_2SO)NO]^+$. The two weak lines have not been positively assigned since the only complex known to give a two line spectrum is the hydroxy complex, and the two weak lines are at slightly higher field than in the spectrum of the hydroxy complex in dimethylsulphoxide.

The pmr spectra of the nitrato complex $[Ru(V(CH_3)_2)_2(NO_3)NO]$ in CD_3CN or $(CD_3)_2SO$ are complicated, and indicate the presence of at least four violurate species. Some of these are clearly solvated complexes, but a satisfactory assignment of the total spectrum could not be achieved.

Discussion

Perhaps surprisingly, the complexes of violurates and dimethylviolurates show many features in common with the complexes of 2,2′-bipyridine and 1,10-phenanthroline. Most obviously the simple Fe(II) and Ru(II) complexes are all highly coloured as a result of intense d–π^* charge transfer bands in a similar region of the visible spectrum [24, 25]. Complexes of the Fe(II) and Ru(II) series are all low spin and the lower oxidation state is very stable to oxidation. Indeed the tris-violurate and tris-polypyridine complexes of Ru(III) and Fe(III) all apparently spontaneously reduce to their Ru(II) and Fe(II) counterparts.

However the complexes of violurate and dimethylviolurate differ substantially from the polypyridine complexes in their stability and their substitutional lability. Vanderwalle *et al.* [26] have reported the stability constants for some first row transition element violurates, which in all instances are many orders of magnitude less than the corresponding stability constants for their bipyridine and phenanthroline counterparts.

The nitrosyl complexes also demonstrate similarities to the analogous bipyridine and phenanthroline complexes. Nitrosyl complexes of both groups of compounds have properties characteristic of highly electrophilic nitrosyl, that is a high NO stretching frequency, and the ability to react with nucleophiles such as hydroxide ion and thiols. The complexes $[Ru(VR_2)_2(Y)NO]ClO_4$ and $[Ru(VR_2)_2(X)NO]$ share with $[Fe(CN)_5NO]^{2-}$ and $[Ru(L–L)_2(X)NO]^{12+}$ {(L–L) is bipyridine or phenanthroline, and X is a monodentate ligand}, a high ν_{NO} stretching frequency. The coordinated NO groups of $[Fe(CN)_5NO]^{2-}$ and $[Ru(bpy)_2(X)NO]^{12+}$ have been shown to react chemically as the nitrosonium ions [21, 23]. The electrophilicity of these nitrosyl complexes may be related to the π-back bonding properties of the bidentate VR_2^- ligands and the monodentate ligand *cis* to the coordinated NO group.

The violurato nitrosyl complexes are, however, much less stable than the polypyridyl nitrosyls particularly in aqueous solution. Complexes such as $[Ru(bpy)_2(Cl)NO]^{2+}$ are stable over a wide pH range even when they are converted to the NO_2^- complex. In contrast the water soluble violurate complexes decompose rapidly at room temperature in neutral or basic solution.

Experimental

Infra-red spectral measurements were made with either a Perkin Elmer 180 or 521 spectrophotometer using nujol mulls, KBr discs or in DMSO using a cell with AgCl windows as appropriate. Ultra-violet and visible spectra were recorded on a Varian-Techtron 635 instrument. ^1H and ^{13}C nmr spectra were recorded using a Bruker WH 90 PFT NMR spectrometer. Spectra were obtained on *ca.* 4×10^{-2} *M* solutions in either $(CD_3)_2SO$, CD_3CN, or D_2O at 306 K. $SiMe_4$ was used as internal reference.

Violuric acid (Fluka) was recrystallised from methanol and dimethylvioluric acid was synthesized according to the literature method [27]. Sodium

violurate and sodium dimethylviolurate were prepared by adding an equimolar amount of NaOH to the corresponding acids. All other chemicals and solvents were used without further purification, unless otherwise stated.

The elemental analyses were performed by the Australian Microanalytical Service.

Synthesis of Complexes

$K[Ru(VH_2)_3]$

Commercial $RuCl_3 \cdot XH_2O$ (1.0 g) was refluxed in ethanol (100 cm^3) for 3 hr to give an emerald green solution and violuric acid (2.6 g) dissolved in hot methanol (100 cm^3) was added. The reaction mixture was refluxed for a further 2 hr and KCl (1 *M*, 5 cm^3) was added. On cooling, black crystals separated and were collected and recrystallised from water. Found: C = 21.6; H = 2.0; N = 19.0%. $[C_{12}H_6N_9O_{12}RuK](H_2O)_{3.5}$ requires C = 21.5; H = 2.0; N = 18.9%.

$K[Ru(V(CH_3)_2)_3]$

This complex could be prepared in a manner similar to the synthesis of $K[Ru(VH_2)_3]$, or by refluxing $K_2[RuCl_5(H_2O)]$ (1.2 g) with sodium dimethylviolurate (2.5 g) in water (200 cm^3) for 3 hr. The volume of the reaction mixture was reduced (*ca.* 25 cm^3) in vacuum and precipitation was induced by the addition of ethanol (100 cm^3). The product was collected and recrystallised from methanol to give dark red crystals. Found: C = 31.6; H = 3.1; N = 17.7%; $[C_{18}H_{18}N_9O_{12}RuK](CH_3OH)$ requires C = 31.5; H = 3.1; N = 17.4%.

$Ba[Ru(VH_2)_2Cl_2]$

$K[Ru(VH_2)_3]$ (1 g) was heated in dil. HCl (5 *M*, 50 cm^3) for 3 hr at 90 °C to give a deep violet solution. Saturated $BaCl_2$ solution (5 cm^3) was then added and the reaction mixture was chilled (−10 °C). The product was collected and recrystallised from dil. HCl (0.1 *M*) and dried in vacuum over P_2O_5. Spectacular gold crystals were obtained. (Violet when crushed). Found: C = 15.5; H = 1.3; N = 13.7; Cl = 11.3%; $[C_8H_4N_6O_8Cl_2RuBa]$ requires C = 15.5; H = 0.7; N = 13.5; Cl = 11.4%.

$K_2[Ru(V(CH_3)_2Cl_2]$

(A). This complex could be prepared by the method described for the synthesis of $[Ru(VH_2)_2Cl_2]^{2-}$ with the exception that saturated KCl solution was used instead of $BaCl_2$ solution. Found: C = 22.7; H = 2.7; Cl = 11.7%; $[C_{12}H_{12}N_6O_8RuCl_2K_2](H_2O)$ requires C = 22.7; H = 2.2; Cl = 11.1%.

(B). A deep blue methanolic solution of $[Ru_5Cl_{12}]^-$ was prepared *in situ* under H_2 [28]. Sodium dimethylviolurate (two molar equivalent with respect to Ru) dissolved in methanol was added under H_2 over 1 hr. The volume of the solution was reduced in vacuum (*ca.* half) and chilled (−10 °C). The blue precipitate was filtered off, washed with ether and dried under N_2. Found: C = 21.8; H = 2.5; Cl = 10.7%; $[C_{12}H_{12}N_6O_8RuCl_2Na_2](H_2O)_4$ requires C = 21.9; H = 3;1; Cl = 10.7%.

$[Ru(VH_2)_2(Cl)NO]$

(A). $Na_2[Ru(NO_2)_4(OH)NO]$ (1.3 g) was reacted with violuric acid (1.1 g) in dil. HCl (5 *M*, 10 cm^3) for 1 hr at 90 °C. On cooling, a yellow precipitate separated which was collected and washed with ice-cold water and dried in vacuum over P_2O_5. Found: C = 19.3; H = 1.3; N = 19.3; Cl = 8.1%; $[C_8H_4N_7O_9ClRu](H_2O)$ requires C = 19.3; H = 1.3; N = 19.7; Cl = 7.1%.

(B). The pH of a saturated aqueous solution of $[Ru(VH_2)_2Cl_2]^{2-}$ was adjusted to ⩽1.5 with conc. HCl and gaseous NO was bubbled through the deep violet solution till it changed to an orange color. The volume of the solution was reduced in vacuum until a yellow precipitate separated and the mixture was chilled (−10 °C). The product was collected and dried in vacuum over P_2O_5, The solubility, ultraviolet and infra-red spectral properties of the product were found to be identical to that of $[Ru(VH_2)_2(Cl)NO]$ prepared by method (A).

$[Ru(V(CH_3)_2)_2(Cl)NO]$

(A). The complex could be prepared from $Na_2[Ru(NO_2)_4(OH)NO]$ (1.3 g) and sodium dimethylviolurate (1.5 g) by the method (A) described for the synthesis of $[Ru(VH_2)_2(Cl)NO]$. Found: C = 26.4; H = 2.5; N = 17.9; Cl = 7.1%; $[C_{12}H_{12}N_7O_9ClRu](H_2O)_{0.5}$ requires C = 26.5; H = 2.4; N = 18.0; Cl = 6.5%.

(B). Alternatively, $[Ru(V(CH_3)_2)_2(Cl)NO]$ could be prepared by passing gaseous NO through a saturated aqueous solution of $[Ru(V(CH_3)_2)_2Cl_2]^{2-}$ as described for the synthesis of $[Ru(VH_2)_2(Cl)NO]$.

(C). This compound could also be prepared from $[Ru(V(CH_3)_2)_2(CH_3CN)NO]ClO_4$ by the following method: $[Ru(V(CH_3)_2)_2(CH_3CN)NO]ClO_4$ (1.0 g) was refluxed in freshly distilled CH_3CN (100 cm^3) and dil. HCl (5 *M*, 5 cm^3) for 30 min. The volume of the solution was reduced in vacuum until a yellow precipitate appeared. The product was collected, washed with water and ethanol, and dried in vacuum over P_2O_5.

The products isolated from method (A), (B) or (C) showed identical spectral and solubility properties.

$[Ru(V(CH_3)_2)_2(NO_3)NO]$

$Na_2[Ru(NO_2)_4(OH)NO]$ (1.3 g) was dissolved in $NaNO_3$ solution (2 *M*, 20 cm^3) and acidified with dil. HNO_3 (5 *M*, 5 cm^3) on a hot-water bath (90 °C). Sodium dimethylviolurate (1.5 g) dissolved in hot

water (50 cm^3) was added over 15 min and the reaction mixture was heated for 1 hr during which time a bright orange complex precipitated. After cooling, the product was collected and washed with water and dried in vacuum at 90 °C for 2 hr. Found: C = 25.6; H = 2.3; N = 20.0%; [$C_{12}H_{12}N_8O_{12}Ru$] requires C = 25.7; H = 2.2; N = 20.0%.

[Ru(V(CH$_3$)$_2$)$_2$(CH$_3$CN)NO] ClO$_4$

[Ru(V(CH$_3$)$_2$)$_2$(NO$_3$)NO] (2.0 g) was refluxed in freshly distilled CH_3CN (100 cm^3) and $HClO_4$ (10 *M*, 1 cm^3) was added dropwise. The volume of the reaction mixture was reduced (*ca.* 15 cm^3) in vacuum and ethanol (50 cm^3) was added to precipitate a yellow complex. The product was collected and recrystallised from CH_3CN and dried in vacuum at 90 °C for 2 hr. Found: C = 26.8; H = 2.3; N = 17.3%; [$C_{14}H_{15}N_8O_{13}RuCl$] requires C = 26.3; H = 2.4; N = 17.5%.

[Ru(V(CH$_3$)$_2$)$_2$((CH$_3$)$_2$SO)NO] ClO$_4$

[Ru(V(CH$_3$)$_2$)$_2$(CH$_3$CN)NO] ClO_4 (0.5 g) was dissolved in freshly distilled $(CH_3)_2SO$ (2 cm^3) with slight warming. Ethanol (50 cm^3) was added to precipitate a red complex which was collected and washed with ethanol and dried in vacuum at 90 °C for 2 hr. Found: C = 25.3; H = 2.7; S = 4.9%; [$C_{14}H_{18}N_7O_{14}SRuCl$] requires C = 24.8; H = 2.7; S = 4.7%.

[Ru(V(CH$_3$)$_2$)$_2$(OH)NO]

[Ru(V(CH$_3$)$_2$)$_2$(CH$_3$CN)NO] ClO_4 (1.0 g) was dissolved in water (500 cm^3) on a hot-water bath (90 °C) and the resultant solution was filtered. On cooling, lemon-yellow precipitate separated which was collected and dried in vacuum over P_2O_5. Found: C = 27.4; H = 2.5; N = 18.7%; [$C_{12}H_{13}N_7O_{10}Ru$]·$(H_2O)_{0.5}$ requires C = 27.4; H = 2.7; N = 18.7%.

[Ru(V(CH$_3$)$_2$)$_2$(H$_2$O)NO] ClO$_4$

A suspension of [Ru(V(CH$_3$)$_2$)$_2$(OH)NO] was acidified with conc. $HClO_4$ (pH ⩽ 1.0) to give pale orange precipitate. The product was collected and washed with water and dried in vacuum over P_2O_5. Found: C = 23.6; H = 2.3; N = 16.2; Cl = 6.3%; [$C_{12}H_{14}N_7O_{14}RuCl$] requires C = 23.4; H = 2.3; N = 15.9; Cl = 5.8%.

[Ru(V(CH$_3$)$_2$)$_2$(H$_2$O)NO] HSO$_4$

[Ru(V(CH$_3$)$_2$)$_2$(NO$_3$)NO] (1.0 g) was refluxed in freshly distilled CH_3CN (50 cm^3) and H_2SO_4 (10 *M*, 1 cm^3) was added dropwise. The volume of the mixture was reduced (*ca.* 10 cm^3) in vacuum and ethanol (50 cm^3) was added to precipitate a yellow complex. The product was collected and washed with ethanol and dried in vacuum at 90 °C for 2 hr. Found: C = 23.6; H = 2.4; N = 16.0; S = 5.2%; [$C_{12}H_{15}N_7O_{14}RuS$] requires C = 23.6; H = 2.4; N = 16.0; S = 4.7%.

[Ru(V(CH$_3$)$_2$)$_2$(C$_5$H$_5$N)NO] ClO$_4$

[Ru(V(CH$_3$)$_2$)$_2$(CH$_3$CN)NO] ClO_4 (0.5 g) was refluxed in freshly distilled CH_3CN (50 cm^3) with C_5H_5N (0.1 cm^3) for 30 min. The volume of the solvent was reduced (*ca.* 20 cm^3 in vacuum and precipitation was induced by the addition of ether (100 cm^3). The product was recrystallised and isolated in a manner similar to that of [Ru(V(CH$_3$)$_2$)$_2$(CH$_3$CN)NO] ClO_4. Found: C = 29.7; H = 2.4; N = 16.2%; [$C_{17}H_{17}N_8O_{13}RuCl$]·$(H_2O)_{0.5}$ requires C = 29.7; H = 2.6; N = 16.3%.

[Ru(V(CH$_3$)$_2$)$_2$(C$_3$H$_4$N$_2$)NO] ClO$_4$

This complex was prepared in a similar way to the preparation of [Ru(V(CH$_3$)$_2$)$_2$(C$_5$H$_5$N)NO]·ClO_4 as described above by using imidazole (0.6 g) instead of pyridine. Found: C = 27.3; H = 2.6; N = 18.8%; [$C_{15}H_{16}N_9O_{13}RuCl$] requires C = 27.0; H = 2.4; N = 18.9%.

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