Generation of the $V(NO)_2{}^+$ Moiety from $VO_4{}^{3-}$ using Hydroxylamine and Pseudo-halide Ions: Synthesis and Electrochemistry of $[V(NO)_2(L\text{–}L)_2]X$ (L–L = 2,2′-bipyridine or 1,10-phenanthroline)†

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Vanadate in aqueous alkali reacted with $NH_2OH{\cdot}HCl$ and X^- (X^- = NCS^-, $N_3{}^-$ or CN^-) ions only in the presence of L–L [L–L = 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)] ligands and at *ca.* 35 °C to yield $[V(NO)_2(L\text{–}L)_2]X$ (X = NCS **1**, N_3 **2** or CN **9**, L–L = phen; X = NCS **3**, N_3 **4** or CN **10**, L–L = bipy). Anion metathesis yields $[V(NO)_2(phen)_2]Y$ (Y = ClO_4 **5** or BPh_4 **6**) and $[V(NO)_2(bipy)_2]Y$ (Y = ClO_4 **7** or BPh_4 **8**). The complexes behave as 1 : 1 electrolytes in methanol, acetonitrile and dimethylformamide and exhibit four-band electronic spectra. The solids are diamagnetic, compatible with the existence of a $\{V(NO)_2\}^6$ moiety in all the complexes. Since the NO ligands occupy *cis* positions, the overall symmetry of the molecules is low, which is supported by the ^1H NMR data of **1** and **3**, which show that two L–L ligands are in different magnetic environments. All the complexes exhibit two successive L–L centred single-electron reductive cyclic responses at negative potentials corresponding to E°_{298} of *ca.* −1.30 and *ca.* −1.50 V *vs.* saturated calomel electrode (SCE), typical for some d^6 systems. At positive potentials, the phen complexes show one metal-centred oxidative cyclic response at E°_{298} *ca.* 0.60 V *vs.* SCE and two irreversible oxidative responses at higher potentials. The bipy complexes, however, show four consecutive irreversible oxidative peaks. In the case of the phen complex **5**, the first oxidative response has been confirmed as metal centred by EPR data after exhaustive coulometry, which shows a typical ^{51}V hyperfine (octet), as well as superhyperfine splitting (nonet) due possibly to the interaction of the unpaired electron with phen nitrogens.

The reaction between tetraoxometalates $MO_4{}^{n-}$ (n = 3, M = V; 2, M = Cr or Mo; 1, M = Mn or Re; 0, M = Os) and hydroxylamine leading to the generation of $M(NO)^{y+}$ moities (y = 1–3) was first reported in 1948[1] and was mentioned only sporadically[2] up to 1970. Thereafter an upsurge in activity[3,4] in this area was noted, mainly due to the interesting electron-transfer property[5a] of the products and their uses, catalytically[6] or stoichiometrically,[6c] in organic synthesis. This type of reaction quite frequently needs the presence of reducing nucleophiles like CN^-,[1,2,4c,e,f,h,l,m] NCS^-,[3a,4a,b,d,g,i] $N_3{}^-$ [refs 4(*b*), 4(*d*), 4(*g*)] or $C_2O_4{}^{2-}$ [refs. 3(*e*), 4(*o*)] ions where $MoO_4{}^{2-}$,[1,3,4d,f] $CrO_4{}^{2-}$,[2a,3a,4a,d,e] $MnO_4{}^-$,[4l] $ReO_4{}^-$,[4b,c,i–k] $VO_4{}^{3-}$ [refs. 2,4(*h*)] or OsO_4 [refs. 3(*a*), 4(*g*), 4(*o*)] is present as substrate. Generally, all the above substrates, besides $ReO_4{}^-$, require an alkaline medium for nitrosylation to occur in the presence of CN^-, but a neutral or slightly acidic medium, in the presence of NCS^-, $N_3{}^-$ or $C_2O_4{}^{2-}$ ions.[3,4] For $ReO_4{}^-$ an alkaline medium is essential for any such reaction to occur irrespective of the presence of anions,[4b,c,i] and this metalate undergoes facile nitrosylation exclusively with NH_2OH,[4j] without the aid of any anionic nucleophile. Molybdate also gives such a reaction in slightly acidic media to yield polymeric species[5b] or discrete monomers isolable in the presence of neutral or anionic organic chelators.[4p] All the above reactions proceed more smoothly in the presence of an excess of NH_2OH[4] than when rather a meagre amount is used,[1–3] affording a higher yield of nitrosyl products in each case and the nature of products remains the same. The case of $VO_4{}^{3-}$ is, however, different. At a low NH_2OH concentration and in the presence of CN^-, a difficult to prepare $V(NO)^{2+}$ was generated[2a,b] in moderate yield; but when excess of NH_2OH was used dinitrosyl products containing the $V(NO)_2{}^{2+}$ moiety were obtained.[4h]

We have now found that facile nitrosylation of $VO_4{}^{3-}$ using an excess of NH_2OH and X^- (X = NCS or N_3) requires the presence of other neutral chelators, possessing an extended π system, of the type L–L [1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy)], and cationic complexes of the type $[V(NO)_2(L\text{–}L)_2]X$ containing the $V(NO)_2{}^+$ moiety [formally vanadium(−I), assuming NO^+ formalism] are obtained. The reaction when repeated with X^- = CN^- also yields $[V(NO)_2(L\text{–}L)_2]CN$. Anion metathesis in each case is possible when the incoming anions are $ClO_4{}^-$ or $BPh_4{}^-$. In the present paper the synthesis, characterisation and electrochemistry of some new‡ cationic dinitrosylvanadium derivatives obtained directly from $VO_4{}^{3-}$ are described. It is noteworthy that NH_2OH in the presence of L–L ligands reduces $VO_4{}^{3-}$ to vanadium(−I). Interestingly, this is the first time that cationic nitrosyl derivatives have been obtained *via* reductive nitrosylation of tetraoxometalates using hydroxylamine.

Results and Discussion

(*a*) *Synthesis, Characterisation and Probable Structure.*— Vanadate ($VO_4{}^{3-}$) in aqueous alkaline solution did not form any coloured species when treated with an excess of $NH_2OH{\cdot}HCl$ and NCS^- or $N_3{}^-$, indicating that reduction as well as nitrosylation had not occurred. However, as soon as L–L ligands, having extended π clouds, *viz.* phen or bipy, are added to the reaction mixture, conversion into nitrosylvanadium products begins and ultimately $[V(NO)_2(phen)_2]X$ (X = NCS

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† *Non-SI unit employed:* G = 10^{-4} T.

‡ While preparing this manuscript we noticed that the cyanide and perchlorate compounds have recently been obtained (though some IR data are a bit different from ours) otherwise using a well known nitrosyl starting material.[7] Our earlier work[4h] constituting the first report of reductive dinitrosylation of $VO_4{}^{3-}$, had, however, not been cited therein.

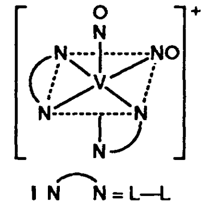
Table 1 Analytical[a] and physical data for the complexes

	Analysis (%)				Selected IR data (cm^{-1})				Solution conductance
Complex	C	H	N	V	ν(NO)	Anion	ν(VN)(NO)	δ(VNO)	Λ_m/ohm^{-1} cm^2 mol^{-1}
1 $[V(NO)_2(phen)_2]NCS$[b]	56.5	2.8	18.4	9.8	1695vs	2085vs	645w	540w	102[c]
	(56.7)	(3.0)	(18.5)	(9.6)	1550vs			500w	
2 $[V(NO)_2(phen)_2]N_3\cdot 2H_2O$	52.2	3.6	22.8	9.5	1705vs	2030vs	650w	565w	107[c]
	(52.5)	(3.7)	(22.9)	(9.3)	1570vs			505w	
3 $(V(NO)_2(bipy)_2]NCS$[b]	52.2	3.2	20.2	10.9	1690vs	2080vs	658w	548w	98[c]
	(52.4)	(3.3)	(20.4)	(10.6)	1550vs			508w	
4 $[V(NO)_2(bipy)_2]N_3\cdot 2H_2O$	47.5	3.9	24.8	10.4	1690vs	2020vs	660w	552w	108[c]
	(47.9)	(4.0)	(25.1)	(10.2)	1584vs			510w	
5 $[V(NO)_2(phen)_2]ClO_4$	50.2	2.7	14.5	9.2	1705vs	1105s (br)	650w	562w	128[d]
	(50.5)	(2.8)	(14.7)	(8.9)	1570vs	625m		504w	
6 $[V(NO)_2(phen)_2]BPh_4$	72.6	4.3	10.5	6.5	1710vs	3060m (br)	648w	548w	123[d]
	(72.9)	(4.5)	(10.6)	(6.4)	1584vs	738sh		500w	
						708sh			
						612m			
7 $[V(NO)_2(bipy)_2]ClO_4$	46.2	3.1	15.9	10.0	1704vs	1100s (br)	656w	556w	132[d]
	(45.9)	(3.1)	(16.1)	(9.7)	1570vs	620m		500w	
8 $[V(NO)_2(bipy)_2]BPh_4$	70.7	4.7	11.3	7.1	1705vs	3074m (br)	640w	558w	125[d]
	(71.2)	(4.9)	(11.3)	(6.9)	1585vs	737sh		504w	
						708sh			
						615m			
9 $[V(NO)_2(phen)_2]CN$	60.1	3.2	19.3	10.5	1695vs	2128w	646w	570w	77[e]
	(60.4)	(3.2)	(19.7)	(10.2)	1560vs	2110w		505w	
10 $[V(NO)_2(bipy)_2]CN$	55.7	3.6	21.5	11.6	1690vs	2130w	648w	570w	72[e]
	(56.1)	(3.6)	(21.8)	(11.3)	1550vs	2110w		508w	

[a] Calculated values are shown in parentheses. [b] S 6.2 (6.0) for complex **1** and 6.9 (6.7%) for **3**. [c] In methanol. [d] In acetonitrile. [e] In dmf.

1 or N_3 **2**) or $[V(NO)_2(bipy)_2]X$ (X = NCS **3** or N_3 **4**) are isolable in crystalline form. The reaction conditions, *viz* temperature (*ca.* 35 °C) and pH (*ca.* 8), are very crucial. All the compounds are air sensitive and show 1:1 electrolytic behaviour[8] in methanol. From their methanol solutions, anion metathesis affords $[V(NO)_2(phen)_2]Y$ (Y = ClO_4 **5** or BPh_4 **6**) or $[V(NO)_2(bipy)_2]Y$ (Y = ClO_4 **7** or BPh_4 **8**) which also show 1:1 electrolytic behaviour in acetonitrile. When instead of NCS^- or N_3^- the reaction is conducted using CN^-, the known compounds $[V(NO)_2(L\text{–}L)_2]CN$ (L–L = phen **9** or bipy **10**), prepared otherwise,[7] are obtained. Interestingly, if the reaction in the presence of CN^- * is conducted at an elevated temperature, reductive nitrosylation starts even in the absence of L–L ligands and, when the latter are added, formally zerovalent, paramagnetic and EPR-sensitive vanadium species $[V(NO)_2(CN)_2(L\text{–}L)]$ † are obtained. Hence, the reductive nitrosylation of VO_4^{3-} using an excess of hydroxylamine and pseudo-halide ions is very fascinating: when the pseudohalide is CN^-, mild reaction conditions afford $V(NO)_2^+$ $[\{V(NO)_2\}^6]$ ‡, while $V(NO)_2^{2+}$ $[\{V(NO)_2\}^5]$ is obtained at elevated temperature; however, when the pseudo-halide is NCS^- or N_3^- the products are obtained only under mild conditions and at higher temperature reaction yields apparently polymeric, non-nitrosyl oxovanadium derivatives.

As usual[4h,7] the nitrosyl groups are in *cis* configuration with respect to each other, which is apparent from two strong ν(NO) vibrational modes at *ca.* 1760 and 1560 cm^{-1} (for exact positions see Table 1), a region in which the neutral $[V(NO)_2(CN)_2(L\text{–}L)]$ complexes also absorb. This is expected insofar as the projected higher electron density of vanadium, consequent upon its lower oxidation state, cannot become a reality due to the overall positive charge of the complex species, which restricts $V_{d_\pi} \rightarrow NO_{(p_\pi)}$ π-back bonding. Notably, a large energy separation (*ca.* 140 cm^{-1}) exists between the two ν(NO) vibrations, in the present case, as well as for our previously reported $M(NO)_2^{2+}$ (M = V or Re) species,[4h,i] compared to a rather small separation (*ca.* 50 cm^{-1}) in some rhenium-dinitrosyl compounds reported earlier.[10,11]



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The water molecules present for the azide salts **2** and **4** are only held in the lattice since DTA and TGA curves show that two molecules of water are lost well below 100 °C (60 °C for both **2** and **4**), endothermically. Since the vanadium-nitrosyl system reported here contains the $\{V(NO)_2\}^6$ moiety, the observed diamagnetism is well expected, insofar as the suggested structure **I** should conform to no higher than C_1 symmetry and hence the molecular orbital (MO) electronic configuration should be[9] $(a'')^2(a')^2(a')^2$.

A comparison of the electronic spectral data for $[V(NO)_2(CN)_4]^{2-}$ as well as its bipy and phen derivatives[4h] with those of the present compounds indicates that the majority of bands of the latter arise from the $V(NO)_2$ core and that the $\{V(NO)_2\}^5$ moiety present in an anion[4h] shows similar spectral features with $\{V(NO)_2\}^6$ present in a cation. The band positions are, however, somewhat altered. Accordingly, and taking into account the low-symmetry field (C_1) in *cis*-dinitrosyls, the lowest-energy band at 750–790 nm in each case can be assigned to a $a' \longrightarrow b_1$ $[d_{(metal)} \longrightarrow \pi^*_{NO}]$ transition, which is Laporte-forbidden ($g \longleftrightarrow g$) and hence of weak intensity. Clearly, the L–L ligands as well as the anions have a considerable effect on the position of this band but no firm and systematic variation in the positional sequence depending on the ligand or anion has

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* However, not in the presence of NCS^- or N_3^-, for which it may be reiterated the reaction temperature of *ca.* 35 °C is very crucial.

† Non-electrolyte in dimethylformamide (dmf) and have superimposable IR spectra with those of authentic samples.[4h]

‡ The numerical superscript indicates the total number of valence electrons in the metal and NO orbitals (see, for example, ref. 9). This notation will be used hereafter.

Table 2 Electronic spectral data of the isolated complexes[a]

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})				
1	772(64)	479(1531)	418(1371)	294(5020)	265 (50 881)[b]
2	762(237)	500(3945)	415(2621)	293(7700)	267 (53 443)[b]
3	764(97)	492(2620)	413(1775)	311(7856)	293 (23 228)[b]
4	765(97)	490(2995)	407(2065)	308(6250)	295 (25 670)[b]
5	760(207)	496(3707)	408(2773)	294(7009)	269 (45 755)[c]
6	750(269)	498(3645)	407(2585)	292(6222)	269 (45 560)[c]
7	762(44)	487(1565)	400(1152)	313(3892)	296 (13 241)[c]
8	766(57)	486(3079)	395(2327)	312(5204)	290 (26 017)[c]
9	790(24)	473(600) [472][c]	408(530)	290(3190)	265 (34 549)[d] [267][c]
10	765(46)	480(988) [485][c]	418(631)	307(3041)	285 (21 996)[d] [303][c]

Corresponding peak positions in acetonitrile: **1**, 763, 475, 383, 294 and 268; **2**, 753, 490, 396, 293 and 263; **3**, 755, 489, 403, 311 and 295; **4**, 769, 489, 398, 308 and 290 nm.

[a] Gaussian analysed; molar absorptivities are shown in the parentheses. [b] In methanol. [c] In acetonitrile. [d] In dmf.

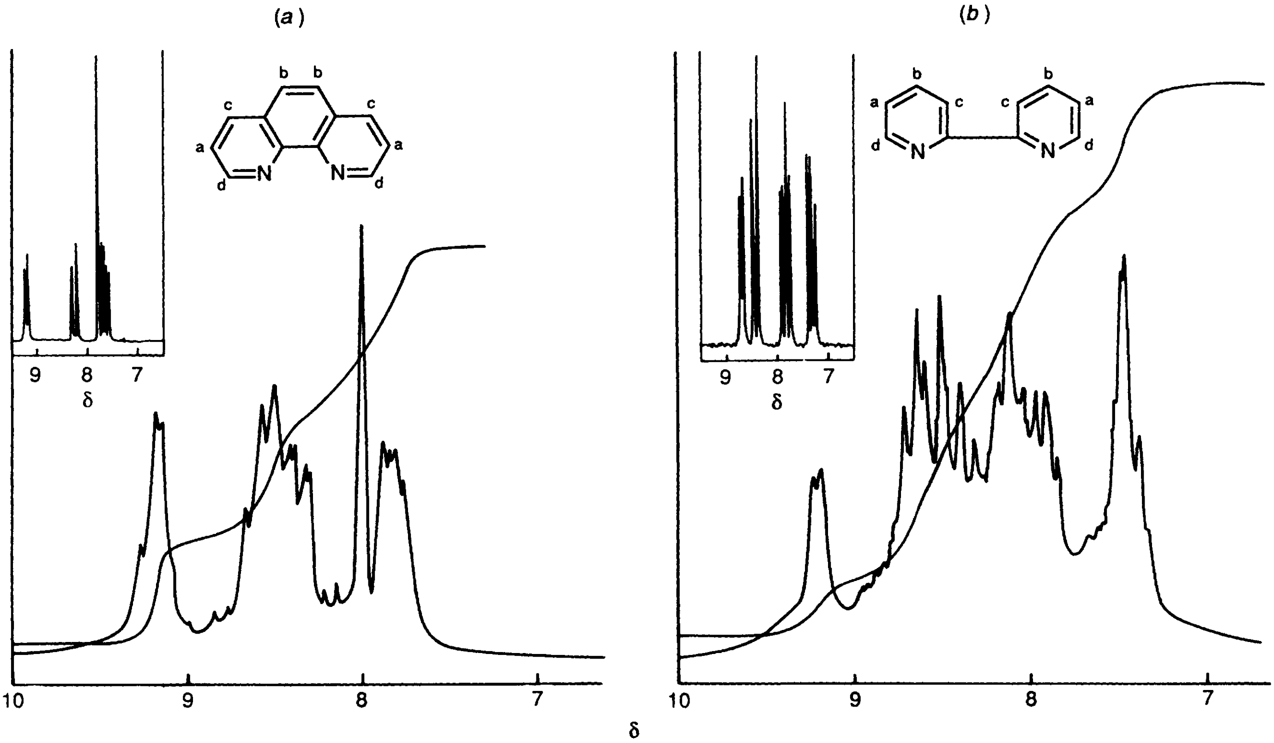

Fig. 1 Proton NMR spectra of (*a*) [V(NO)$_2$(phen)$_2$]NCS and (*b*) [V(NO)$_2$(bipy)$_2$]NCS in CD$_3$OD. The insets show the spectra of unco-ordinated phen and bipy

been noted. The next three bands (Table 2) in order of increasing energy can be assigned to a′ $\longrightarrow$ a′, a′ $\longrightarrow$ a′ and a′ $\longrightarrow$ a″ transitions.[9]

Unco-ordinated bipy or phen exhibits a characteristic $\pi \longrightarrow \pi^*$ transition at 280 and 260 nm, respectively. Interestingly, in the present complexes **1**–**10**, this transition undergoes a pronounced bathochromic shift which parallels the profound shift of the redox potential of co-ordinated compared to unco-ordinated bipy or phen [see section (*b*)].

The C_1 symmetry exhibited by the complexes means that the L–L ligands will have different magnetic environments and is demonstrated by the ^{1}H NMR spectra of both the phen and bipy complexes in CD$_3$OD. Unco-ordinated phen exhibits[12] a double doublet at δ 7.62 (a, 2 H), two pairs of doublets, one at 8.26 (c, 2 H) and the other at 9.21 (d, 2 H), and a singlet at 7.80 (b, 2 H) [Fig. 1(*a*)], whereas for complex **1** we observe a multiplet at δ 7.80 (a, 4 H), a singlet at 7.97 (b, 2 H), an overlapping multiplet at 8.36 {6 H [b, (2 H) + c, (4 H)]} and a quartet at 9.22 (d, 4 H). Strangely, the downfield shift of protons d [Fig. 1(*a*)] is less pronounced than for the others. Similarly for unco-ordinated bipy[12] four groups of multiplets each representing 2 H are observed at δ 7.32 (a), 7.84 (b), 8.44 (c) and 8.70 (d), changing to a multiplet at δ 7.46 (a, 4 H), two highly resolved multiplets at 8.04 (b, 4 H) and 8.52 {6 H [c, (4 H) + d, (2 H)]} and a doublet at 9.20 (d, 2 H) for complex **3**, showing a more pronounced downfield shift of the proton resonances than that observed for the phen complex **1** [Fig. 1(*b*)].

(*b*) *Electrochemistry*.—All the complexes **1**–**10** in acetonitrile (dmf for CN$^-$ salts) exhibit two successive one-electron (ascertained by coulometry) reductive cyclic* responses (Fig. 2) at potentials around -1.28 and -1.52 V *vs.* saturated calomel electrode (SCE). The couples may be assigned to electron

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* Reversibility of the responses was assigned according to ΔE_p (see Table 3) of *ca.* 60–80 mV and $i_c/i_a \approx 1$, where i_c = cathodic current and i_a = anodic current.

Table 3 Cyclic voltammetric data for the isolated complexes in the range of + 1.8 to − 1.8 V in MeCN–NEt$_4$ClO$_4$ at a scan rate of 50 mV s^{-1}

	Reversible responses[a]/V									
	ΔE_p = 80 mV						ΔE_p = 60 mV			Other responses
Complex	E_{pa}	E_{pc}	E°_{298}	E_{pa}	E_{pc}	E°_{298}	E_{pa}	E_{pc}	E°_{298}	E_{pa}/V
1	−1.24	−1.32	−1.28	−1.50	−1.58	−1.54	0.70	0.64	0.67	1.40,
	(−1.62)	(−1.70)	(−1.66)	(−1.88)	(−1.96)	(−1.92)	(0.32)	(0.26)	(0.29)	1.02
2	−1.26	−1.34	−1.30	−1.50	−1.58	−1.54	0.60	0.54	0.57	1.32,
	(−1.64)	(−1.72)	(−1.68)	(−1.88)	(−1.96)	(−1.92)	(0.22)	(0.16)	(0.19)	0.98
5	−1.26	−1.34	−1.30	−1.50	−1.58	−1.54	0.64	0.58	0.63	1.34,
	(−1.64)	(−1.72)	(−1.68)	(−1.88)	(−1.96)	(−1.92)	(0.26)	(0.20)	(0.25)	0.98
6	−1.26	−1.34	−1.30	−1.50	−1.58	−1.54	0.63	0.57	0.60	1.38,
	(−1.64)	(−1.72)	(−1.68)	(−1.88)	(−1.96)	(−1.92)	(0.25)	(0.19)	(0.22)	0.94
9[b]	−1.22	−1.30	−1.26	−1.48	−1.56	−1.52	0.72	0.66	0.69	1.42,
	(−1.67)	(−1.75)	(−1.71)	(−1.93)	(−2.01)	(−1.97)	(0.27)	(0.21)	(0.24)	1.04

	Reversible responses/V (ΔE_p = 80 mV)						Other responses
	E_{pa}	E_{pc}	E°_{298}	E_{pa}	E_{pc}	E°_{298}	E_{pa}/V
3	−1.22	−1.30	−1.26	−1.46	−1.54	−1.50	1.32, 1.08, 0.88, 0.62
	(−1.60)	(−1.68)	(−1.64)	(−1.84)	(−1.92)	(−1.88)	
4	−1.22	−1.30	−1.26	−1.46	−1.54	−1.50	1.36, 1.06, 0.80, 0.58
	(−1.60)	(−1.68)	(−1.64)	(−1.84)	(−1.92)	(−1.88)	
7	−1.22	−1.30	−1.26	−1.48	−1.56	−1.52	1.28, 1.06, 0.85, 0.64
	(−1.60)	(−1.68)	(−1.64)	(−1.86)	(−1.94)	(−1.90)	
8	−1.22	−1.30	−1.26	−1.48	−1.56	−1.52	1.30, 1.06, 0.86, 0.64
	(−1.60)	(−1.68)	(−1.64)	(−1.86)	(−1.94)	(−1.90)	
10[b]	−1.20	−1.28	−1.24	−1.44	−1.52	−1.48	—, 1.14, 0.94, —
	(−1.65)	(−1.73)	(−1.69)	(−1.89)	(−1.97)	(−1.93)	

[a] Values *vs.* ferrocene–ferrocenium are shown in parentheses. [b] In dmf.

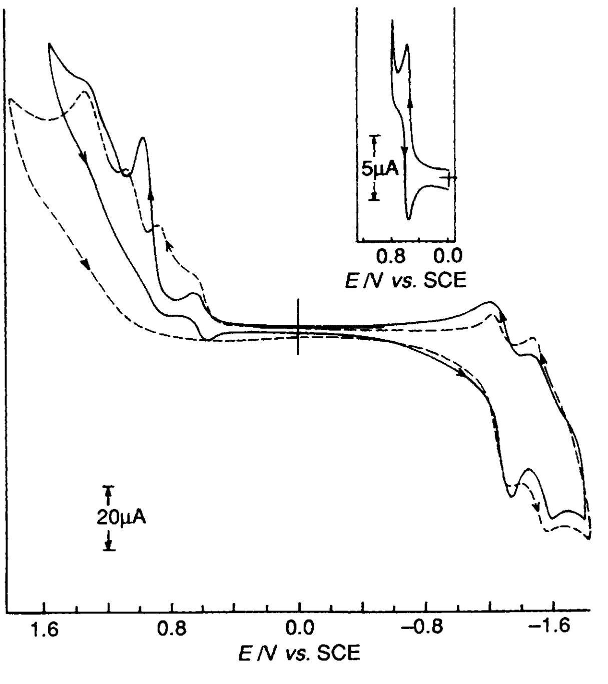

Fig. 2 Cyclic voltammograms of [V(NO)$_2$(phen)$_2$]ClO$_4$ (——) and [V(NO)$_2$(bipy)$_2$]NCS (– – – –) in MeCN–NEt$_4$ClO$_4$ at a scan rate of 50 mV s^{-1}. The inset shows the segmented oxidative cyclic response of [V(NO)$_2$(phen)$_2$]ClO$_4$

transfer to the ligand (bipy or phen)-localised redox MOs[13] which is considered typical for the d^6 metal ions Fe^{2+} and Ru^{2+}, and, here, for the {V(NO)$_2$}^{6} core. The presence of two such responses indicates sequential reduction of two phen or bipy molecules. The UV/VIS spectra of the reduced species after coulometry beyond each redox couple (for the exact position of the couples *vs.* SCE and relative to ferrocene–ferrocenium, see Table 3) clearly shows a growth and then a gradual increase in intensity of the bands of reduced bipy or phen around 300 nm for all the [V(NO)$_2$(L–L)$_2$]$^+$ complexes, a trend reported to be typical for the above type of L–L localised redox MOs.[14–17] So the entire process at the negative potentials can be described by equations (1) and (2). Uncomplexed bipy

$$[V(NO)_2(L\text{–}L)_2]^+ + e^- \rightleftharpoons [V(NO)_2(L\text{–}L)(L\text{–}\dot{L})] \quad (1)$$

$$[V(NO)_2(L\text{–}L)(L\text{–}\dot{L})] + e^- \rightleftharpoons [V(NO)_2(L\text{–}\dot{L})_2]^- \quad (2)$$

and phen exhibit E_{pc} at −2.16[18] and −2.10 V[19] *vs.* SCE, respectively. The anodic shift of the E_{pc} values of these ligands is commensurate with the lowering in energy of the $\pi \longrightarrow \pi^*$ transition after metal co-ordination.

When scanned at positive potentials the phen and bipy complexes behave differently: while the phen complexes show a reversible cyclic response at E°_{298} *ca.* 0.60 V *vs.* SCE (0.22 V *vs.* ferrocene–ferrocenium) and two other irreversible oxidative waves, the bipy complexes show four consecutive irreversible oxidative responses. Exhaustive electrolysis (coulometry) of the phen complex **5** at a controlled potential (+0.80 V *vs.* SCE) resulted in a charge release of 1 F per mol of complex, confirming a single-electron oxidation for the reversible response. That the oxidation occurs at the metal centre is confirmed by the X-band EPR spectrum of a coulometrically oxidised solution of complex **5**. The spectrum shows a well defined octet which arises from hyperfine coupling of the unpaired electron [{V(NO)$_2$}^{5}] with the spin-active ^{51}V nucleus ($I = \frac{7}{2}$), at 298 K with $\langle g \rangle_{solution}$ = 1.99. The octet comprises irregularly spaced $\langle A \rangle$(^{51}V) tensors from 85 to 110 G (Fig. 3). Interestingly, all the vanadium hyperfine lines are further split into a nonet (the size of the $\langle A \rangle$ tensors varying from *ca.* 5 to 7 G) due to the superhyperfine interaction of the unpaired electron with the four ^{14}N of the two phen molecules, indicating that besides the contribution of metal d atomic orbitals, the highest occupied molecular orbital (HOMO) also has a reasonable contribution from suitable phen molecular

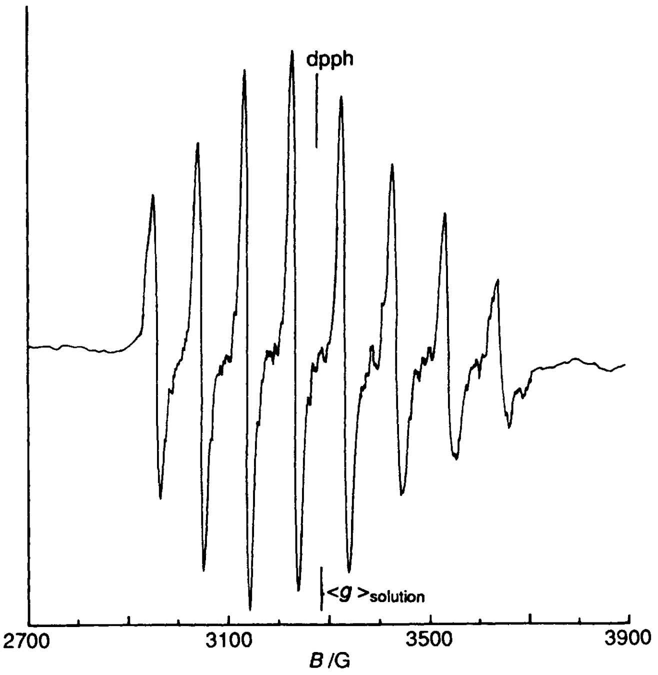

Fig. 3 The X-band EPR spectrum of a coulometrically oxidised solution of $[V(NO)_2(phen)_2]ClO_4$ in acetonitrile at 298 K; dpph = diphenylpicrylhydrazyl

orbitals. By inference, the first oxidation at E_{pa} *ca.* +0.62 V for the bipy complexes can be considered to be metal centred and hence is attributable to the electrochemical reaction (3). The

$$\underset{V\{(NO)_2\}^6}{[V(NO)_2(L\text{–}L)_2]^+} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \underset{\{V(NO)_2\}^5}{[V(NO)_2(L\text{–}L)_2]^{2+}} \qquad (3)$$

second oxidative (irreversible) step of both phen and bipy complexes was found to be single stepped in $MeCN\text{–}NEt_4ClO_4$ as confirmed by coulometry, and the electrochemical process involved has been diagnosed as metal centred from the significant shift of the electronic spectral bands of the oxidised species * from those of the parents. So, the second oxidation step may represent the electrochemical process (4).

$$[V(NO)_2(L\text{–}L)_2]^{2+} \xrightarrow{-e^-} [V(NO)_2(L\text{–}L)_2]^{3+} \qquad (4)$$

Another interesting observation of the electrochemical work is that the reversible L–L centred reductions at negative potentials are less sensitive to the addition of extra ligand during the cyclic voltammetric recording than are the metal-centred oxidations at positive potentials. So it may be argued that at positive potentials the complexes become more labile and undergo solvent-assisted dissociation.[20] In this context no attempt has been made to attribute the third oxidative response of the phen and third and fourth responses of the bipy complexes.

Experimental

Materials and Methods.—All the reagents required for compound preparation were of analytical grade. For physicochemical studies the analytical grade solvents were further purified by literature methods.[21] Water of high purity was obtained by double distillation from $KMnO_4$ of deionised water. The supporting electrolyte, tetraethylammonium perchlorate, was prepared using the literature method.[22] Dinitrogen for electrochemical and thermoanalytical work was purified by passage through an alkaline dithionite reducing solution. Chemically pure grade ferrocene from Sigma Chemical Company was used directly.

Infrared spectra (4000–200 cm^{-1}) were recorded as KBr pellets on a Perkin Elmer 597 spectrophotometer and electronic spectra on a Hitachi U-3400 UV/VIS/NIR spectrophotometer. The solution conductances were measured with a Systronics (India) model 304 digital conductivity meter. Thermoanalyses were made on a Shimadzu DT 30 thermoanalyser. Voltammetric measurements were done with a PAR model 370-4 electrochemistry system: model 174A polarographic analyser, model 175 universal programmer, model RE 0074 XY recorder, model 173 potentiostat and model 179 digital coulometer. All experiments were made at 298 K under a dinitrogen atmosphere in a three-electrode cell using a stout platinum wire as the working electrode, a platinum foil as the auxiliary electrode, and a saturated calomel reference electrode. For coulometry a platinum-wire gauze working electrode was used. The potentials reported are uncorrected for junction contribution. Proton NMR spectra were obtained on a Varian EM 390 (90 MHz) spectrometer using $SiMe_4$ as standard, the X-Band ESR spectrum on a Varian E-109C spectrometer fitted with a quartz Dewar for measurements at low temperatures. Elemental analyses were made on a Perkin Elmer model 240C elemental analyser and vanadium was estimated gravimetrically as V_2O_5.

Preparation of Complexes.—$[V(NO)_2(L\text{–}L)_2]NCS$ (L–L = phen **1** *or* bipy **3**). In a solution of $NH_2OH{\cdot}HCl$ (15.2 g, 218.7 mmol) in water (140 cm^3) was dissolved $NaVO_3{\cdot}H_2O$ (1 g, 7.14 mmol). Ammonium thiocyanate (11.2 g, 147.1 mmol) and an ethanolic (5 cm^3) solution of L–L [phen (2.83 g, 14.29 mmol) or bipy (2.23 g, 14.29 mmol)] were added with stirring. A hot solution of NaOH (6 mol dm^{-3}) was added to render the solution just alkaline (pH ≈8). The solution was kept at 35 °C until it became deep red. It was then filtered and the filtrate was left for 24 h. A red precipitate was obtained for complex **1**, which was filtered off, washed thoroughly with a 1% aqueous solution of NH_4SCN and finally with water and vacuum dried. The complex was crystallised from dmf–ethanol under dinitrogen and kept over P_2O_5. Dark red shiny microcrystals were obtained for **3**, which were filtered off, washed with 1% NH_4SCN solution and finally with water, and dried under reduced pressure over P_2O_5. Attempted crystallisation destroyed the shiny crystalline nature and so the original crystals were used directly. Yields: **1**, 1.2 (31.7); **3**, 1.1 g (32.0%).

$[V(NO)_2(L\text{–}L)_2]N_3{\cdot}2H_2O$ (L–L = phen **2** *or* bipy **4**). The above procedure was applied, employing NaN_3 (10 g, 153.8 mmol) instead of NH_4SCN. Dark red microcrystals were obtained in each case, which were filtered off, washed repeatedly with 1% NaN_3 solution and finally with water, and dried over P_2O_5 *in vacuo*. Attempted crystallisation destroyed the crystalline nature so the original crystals were used directly. Yields: **2**, 1.42 (36.2); **4**, 1.09 g (30.4%).

$[V(NO)_2(L\text{–}L)_2]ClO_4$ (L–L = phen **5** *or* bipy **7**). Freshly prepared crystalline $[V(NO)_2(L\text{–}L)_2]X$ (0.22 mmol) (L–L = phen or bipy; X = CN, SCN or N_3) was dissolved in methanol (10 cm^3). An aqueous solution (5 cm^3) of $NaClO_4$ (0.03 g, 0.245 mmol) was added and the solution was diluted by water (50 cm^3) and kept overnight. A red precipitate was filtered off, washed with water and dried under reduced pressure over P_2O_5. Yields: **5**, 0.1 (79.6); **7**, 0.081 g (70.4%).

$[V(NO)_2(L\text{–}L)_2]BPh_4$ (L–L = phen **6** *or* bipy **8**). Freshly prepared crystalline $[V(NO)_2(L\text{–}L)_2]X$ (0.22 mmol) (L–L = phen or bipy; X = CN, SCN or N_3) was dissolved in methanol (10 cm^3). A methanolic solution (5 cm^3) of $NaBPh_4$ (0.08 g, 0.234 mmol) was added. A red precipitate was filtered off, washed with methanol and dried under reduced pressure over P_2O_5. Yields: **6**, 0.14 (80.5); **8**, 0.114 g (69.8%).

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* For instance, with complex **5**, the band at 760 nm first shifts to 730 nm after the first oxidation and then to 725 nm after the second oxidation. Another characteristic band shift on sequential oxidation is of the band at 496 nm, which shifts to 500 nm after the first and to 510 nm after the second oxidation.

[V(NO)$_2$(L–L)$_2$]CN (L–L = phen **9** *or* bipy **10**). The same method as described for complexes **1** and **3** was followed using KCN (9.6 g, 174.4 mmol) instead of NH$_4$SCN. A red precipitate was obtained in each case, which was filtered off, washed thoroughly with a 1% aqueous solution of KCN and finally with water and dried *in vacuo*. The solid was purified by crystallisation from dmf–ethanol under dinitrogen and kept over P$_2$O$_5$. Yields: **9**, 1.45 (40.8); **10**, 1.36 g (42.4%).

The water solubility of all complexes **1–10** and the intense colour of the mother-liquors after the isolation of the products, indicate that other products remain in solution. Due to the inherent instability of the compounds, however, they could not be recovered.

Acknowledgements

Financial assistance from the University Grants Commission, New Delhi is gratefully acknowledged. Our sincere thanks go to Professor A. Chakravorty (Indian Association for the Cultivation of Science, Calcutta) for EPR facilities and to Professor N. Ray Chaudhuri of the same Institute for the thermoanalytical work. We thank the Alexander von Humboldt Foundation for the donation of the infrared spectrophotometer (PE 597) used.

References

1 W. Hieber, R. Nast and G. Gehring, *Z. Anorg. Allg. Chem.*, 1948, **256**, 169.

2 (*a*) W. P. Griffith, J. Lewis and G. Wilkinson, *J. Chem. Soc.*, 1959, 872, 1632; (*b*) S. Jagner and N. Vannerberg, *Acta Chem. Scand.*, 1970, **6**, 24; (*c*) D. H. Svedung and N. Vannerberg, *Acta Chem. Scand.*, 1968, **22**, 1551.

3 (*a*) S. Sarkar and A. Müller, *Z. Naturforsch., Teil B*, 1978, **38**, 1953; (*b*) K. Wieghardt, U. Quilitzch, B. Nuber and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1978, **90**, 381; (*c*) K. Wieghardt, W. Holzhach and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 548; (*d*) K. Wieghardt, G. B. Dahman, W. Swiridoff and W. Weiss, *Inorg. Chem.*, 1983, **22**, 1221; (*e*) A. Müller, S. Sarkar, N. Mohan and R. G. Bhattacharyya, *Inorg. Chim. Acta*, 1980, **45**, L245.

4 (*a*) R. G. Bhattacharyya, G. P. Bhattacharjee and P. S. Roy, *Inorg. Chim. Acta*, 1981, **54**, L263; (*b*) R. G. Bhattacharyya and P. S. Roy, *J. Coord. Chem.*, 1982, **12**, 129; *Transition Met. Chem.*, 1982, **7**, 285; *Indian J. Chem., Sect. A*, 1983, **22**, 111; (*c*) R. G. Bhattacharyya and P. S. Roy, *Transition Met. Chem.*, 1984, **9**, 281; (*d*) R. G. Bhattacharyya and G. P. Bhattacharjee, *J. Chem. Soc., Dalton Trans.*, 1983, 1593; *Polyhedron*, 1983, **2**, 1221; (*e*) R. G. Bhattacharyya, G. P. Bhattacharjee and N. Ghosh, *Polyhedron*, 1983, **2**, 543; (*f*) R. G. Bhattacharyya, G. P. Bhattacharjee and A. M. Saha, *Transition Met. Chem.*, 1983, **8**, 255; *Polyhedron*, 1985, **4**, 583; (*g*) R. G. Bhattacharyya and A. M. Saha, *Inorg. Chim. Acta*, 1983, **77**, L81; *J. Chem. Soc., Dalton Trans.*, 1984, 2085; *Transition Met. Chem.*, 1987, **12**, 85; (*h*) R. G. Bhattacharyya, P. S. Roy and A. K. Dasmahapatra, *J. Organomet. Chem.*, 1984, **267**, 293; (*i*) R. G. Bhattacharyya and P. S. Roy, *Inorg. Chim. Acta*, 1984, **87**, 99; (*j*) R. G. Bhattacharyya, P. S. Roy and A. K. Dasmahapatra, *J. Chem. Soc., Dalton Trans.*, 1988, 793; (*k*) R. G. Bhattacharyya, A. K. Dasmahapatra and P. S. Roy, *Proc. Indian Acad. Sci. Sect. A*, 1989, **101**, 273; (*l*) R. G. Bhattacharyya, N. Ghosh and G. P. Bhattacharjee, *J. Chem. Soc., Dalton Trans.*, 1989, 1963; (*m*) R. G. Bhattacharyya, N. Ghosh and A. M. Saha, *Polyhedron*, 1989, **8**, 2897; (*n*) R. G. Bhattacharyya, M. Mallik and P. N. Ghosh, *Inorg. Chim. Acta*, 1990, **168**, 141; (*o*) R. G. Bhattacharyya, A. M. Saha, P. N. Ghosh, M. Mukherjee and A. K. Mukherjee, *J. Chem. Soc., Dalton Trans.*, 1991, 501; (*p*) R. G. Bhattacharyya and S. Ghosh, *Indian J. Chem., Sect. A*, 1991, **30**, 35.

5 (*a*) J. H. Enemark and R. D. Feltham, *Proc. Natl. Acad. Sci. USA*, 1972, **60**, 3534; (*b*) S. Zhang, D. Liao, M. Shao and Y. Tang, *J. Chem. Soc., Chem. Commun.*, 1986, 835.

6 (*a*) E. A. Zuech, W. B. Hughes, D. H. Kubicek and E. T. Kittleman, *J. Am. Chem. Soc.*, 1970, **92**, 528, 532; (*b*) S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc.*, 1971, **93**, 3068; (*c*) K. K. Pandey, *Coord. Chem. Rev.*, 1983, **51**, 69.

7 R. Srivastava and S. Sarkar, *Inorg. Chim. Acta*, 1990, **176**, 27.

8 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

9 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.

10 M. Freni, D. Giusto and V. Valenti, *Gazz. Chim. Ital.*, 1964, **94**, 797.

11 G. LaMonica, M. Freni and S. Cenini, *J. Organomet. Chem.*, 1974, **71**, 57.

12 *Handbook of Proton-NMR spectra and Data*, Asahi Research Center Co. Ltd. Tokyo, Academic Press, New York, 1985, vol. 4.

13 D. E. Morris, K. W. Hanck and M. K. DeArmond, *J. Am. Chem. Soc.*, 1983, **105**, 3032.

14 P. S. Braterman, J. I. Song and R. D. Peacock, *Inorg. Chem.*, 1992, **31**, 555.

15 C. N. Elliott, *J. Chem. Soc., Chem. Commun.*, 1980, 261.

16 G. A. Heath, L. J. Yellowlees and P. S. Braterman, *J. Chem. Soc., Chem. Commun.*, 1981, 287.

17 G. Heath, L. Yellowlees and P. Braterman, *Chem. Phys. Lett.*, 1982, **92**, 646.

18 J. L. Kahl, K. W. Hanck and K. DeArmond, *J. Phys. Chem.*, 1978, **82**, 540.

19 N. E. Tokel-Takvoryan, R. E. Hemingway and A. J. Bard, *J. Am. Chem. Soc.*, 1973, **95**, 6582.

20 A. M. Bond and R. Colton, *Inorg. Chem.*, 1976, **15**, 2036.

21 D. D. Perrin, W. L. F. Armerego and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon, New York, 1966.

22 S. Goswami, A. R. Chakravarty and A. Chakravorty, *Inorg. Chem.*, 1982, **21**, 2737.

Received 20*th October* 1992; *Paper* 2/05595C