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REDUCTIVE NITROSYLATION OF TETRAOXOMETALLATES

XIII *. GENERATION OF $\{V(NO)_2\}^{2+}$ MOIETY: SYNTHESIS OF $[V(NO)_2(CN)_4]^{2-}$ AND $[V(NO)_2(CN)_2(L–L)]$ (L–L = 2,2′-BIPYRIDINE AND 1,10-PHENANTHROLINE) DIRECTLY FROM VO_4^{3-} IN AQUEOUS-AEROBIC MEDIA

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Summary

The vanadium(0) dinitrosyl complex $[V(NO)_2(CN)_4]^{2-}$ containing $\{V(NO)_2\}^{2+}$ moiety is generated for the first time via reductive nitrosylation of VO_4^{3-} with NH_2OH and CN^- in an alkaline medium. The complex anion reacts with L–L [L–L = 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen)] in an aqueous medium to give $[V(NO)_2(CN)_2(L–L)]$. The complexes show characteristic IR bands and paramagnetism, as expected for a system containing a single unpaired electron. They give interesting EPR signals, with g_{av} close to 2.0.

There is increasing interest in transition metal nitrosyl derivatives owing to their many catalytic uses [2], pollution-controlling properties [3] and unusual electron transfer properties [4]. We have recently described easy methods for reductive nitrosylation of CrO_4^{2-} [5], MoO_4^{2-} [6], ReO_4^- [7] and OsO_4 [8] and provided a virtually single step synthesis of the hitherto unknown cyano-, thiocyanato- and azido-nitrosyl derivatives of those metal ions in aqueous-aerobic media. The report of Wilkinson and his co-workers [9] of the synthesis of $K_5[V(NO)(CN)_5]$ from VO_4^{3-} and CN^- in an alkaline medium using $NH_2OH \cdot HCl$ as the source of NO group was subsequently modified by structure analysis by Jagner et al. [10], who reformulated the complex as $K_3[V(NO)(CN)_5] \cdot 2H_2O$. Müller et al. [11] obtained an interesting complex, $K_4[V(NO)(CN)_6]$ by conducting the nitrosylation reaction in H_2S medium, and this product was characterised structurally [12]. Starting from the latter compound, Srivastava et al. [13] succeeded in preparing some L–L derivatives, viz. $K_2[V(NO)(CN)_4(L–L)]$ (L–L = 2,2′-bipyridine (bipy) and 1,10-phenanthroline

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* For part XII see ref. 1.

(phen)). Sarkar et al. [14] carried out a redox reaction between $K_3[V(NO)(CN)_5] \cdot 2H_2O$ and L–L and claimed to have isolated cationic dinitrosyl derivatives of the type $[V(NO)_2(L\text{–}L)_2]^+$, apparently containing $\{V(NO)_2\}^+$ (and hence the $\{V^{VI}(NO)_2\}$) moiety).

Direct reductive nitrosylation of VO_4^{3-} to give dinitrosylvanadium species is still unknown. The great majority of the dinitrosylvanadium complexes reported previously have been derived from η^5-cyclopentadienyl half sandwich compounds [15]. Some dinitrosyl derivatives of vanadium(−I) have also recently been prepared [16] from the parent polymeric trinitrosyl complex $[V(NO)_3Cl_2]_n$, which was obtained by passing NO on VCl_4 [17]. We describe below a single pot and virtually a single step synthesis of the hitherto unknown dinitrosyl complex anion, $[V(NO)_2(CN)_4]^{2-}$ as its K salt, as well as neutral $[V(NO)_2(CN)_2(L\text{–}L)]$ complexes, directly from VO_4^{3-} in aqueous and aerobic medium. These products evidently contain the previously unknown $\{V(NO)_2\}^5$ (i.e. $\{V(NO)_2\}^{2+}$) species; in fact this is the first report of any $\{M(NO)_2\}^5$ species.

Results and discussion

Our repetition of the syntheses described by Wilkinson et al. [9] and Jagner et al. [10] revealed that the nitrosylation reaction did not proceed smoothly, and isolation of the pure complex ($K_3[V(NO)(CN)_5]$) was rather difficult, possibly because the method described involved use of a rather small amount of $NH_2OH \cdot HCl$ (3 times the molar amount of VO_4^{3-}). This was possibly realised by Sharpe who, in a review of cyanonitrosyl complexes, commented that a study on the stoichiometry of the VO_4^{3-}–CN^-–NH_2OH would be of interest [18]. Using an excess of $NH_2OH \cdot HCl$ we found that the reaction proceeded quite smoothly, but to the dinitrosylation state; $K_2[V(NO)_2(CN)_4] \cdot xH_2O$ (I) was easily isolated, but it was almost impossible to obtain it analytically pure because the last traces of KCl could not be removed by fractional crystallisation, the solubility of the complex being almost identical with that of KCl, ion exchange chromatography, or even chromatography through suitable Sephadex columns. The complex is insoluble in all organic solvents and even the aqueous solution is not very resistant to oxidative decomposition if kept for a longer time in order to bring about slow crystallisation, even under an inert atmosphere. However, a freshly made solution of the potassium salt of the cyanodinitrosyl complex on treatment with ligands L–L gives a good yield of the analytically pure L–L derivatives, viz. $[V(NO)_2(CN)_2(L\text{–}L)] \cdot H_2O$ (II and III).

The dinitrosyl complex anion, as expected for NO groups occupying *cis* positions, shows two strong $\nu(NO)$ IR bands at 1650 and 1520 cm^{-1}. (The $\nu(NO)$ band of $K_3[V(NO)(CN)_5]$ has been reported at 1530 cm^{-1} [10] and at 1575 cm^{-1} [9]), and in the neutral $[V(NO)_2(CN)_2(L\text{–}L)]$ complexes these two strong bands are observed at 1680 and 1540 cm^{-1}. All the dinitrosyl complexes contain a split $\nu(CN)$ band around 2100 cm^{-1} (see the Experimental section). The L–L compounds are monomeric and non-electrolytes in CH_3CN solution.

All the dinitrosyl complexes reported here are $\{V(NO)_2\}^5$ systems (assuming NO^+ formalism [19] the oxidation state of vanadium must be zero) and such a nitrosyl species should possess one unpaired electron, and this is confirmed by the observed magnetic moment of the L–L derivatives (μ_{eff} 1.5 BM for II and 1.6 BM for III at 298 K). The magnetic moment of the complex anion is somewhat low

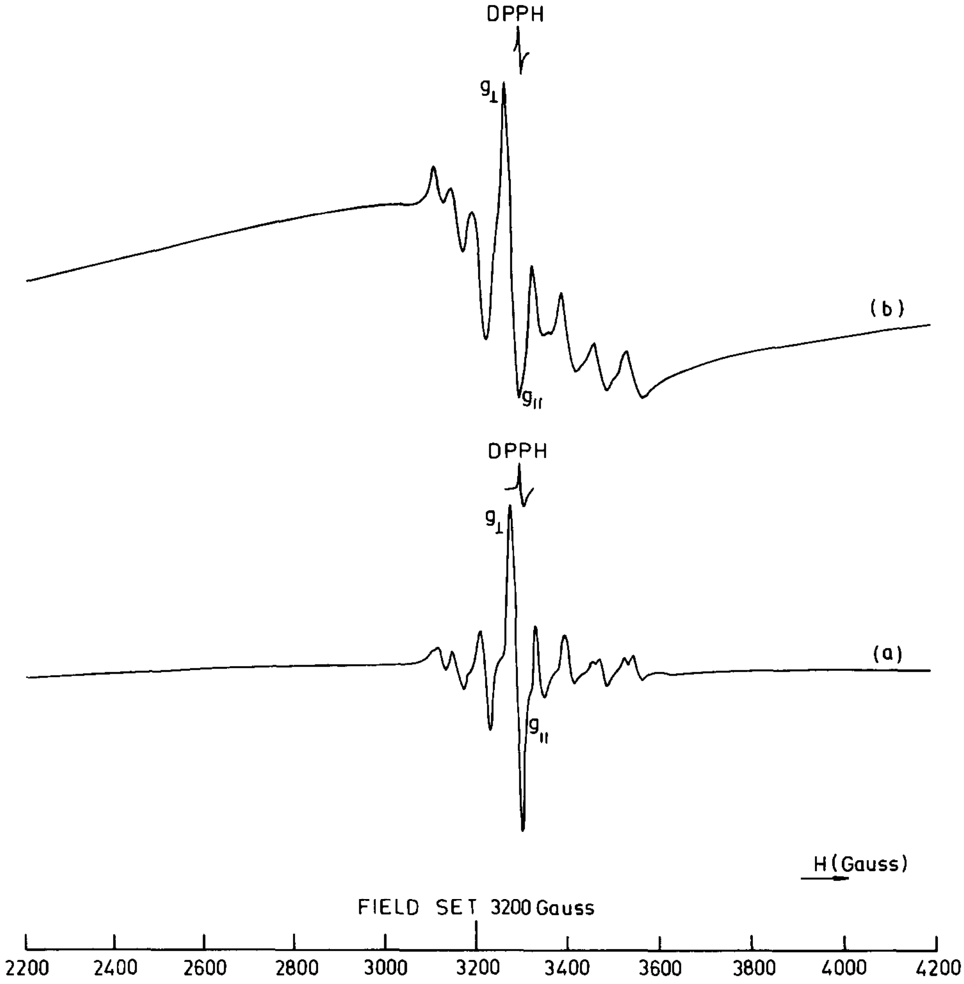

Fig. 1. X-band EPR spectra of (a) $[V(NO)_2(CN)_2(bipy)]\cdot H_2O$ and (b) $[V(NO)_2(CN)_2(phen)]\cdot H_2O$ at liquid nitrogen temperature.

TABLE 1

EPR DATA FOR $[V(NO)_2(CN)_2(L\text{-}L)]\cdot H_2O$ COMPLEXES AT ROOM TEMPERATURE AND LIQUID NITROGEN TEMPERATURE

Complexes	Temperature (K)	g_s	$g_\perp$ [a]	$g_\parallel$ [a]	$\langle A\rangle_V$(G) [b]
$[V(NO)_2(CN)_2(bipy)]\cdot H_2O$	298	2.00	2.01	1.98	50–90
$[V(NO)_2(CN)_2(bipy)]\cdot H_2O$	80	1.99	2.00	1.97	55–75
$[V(NO)_2(CN)_2(phen)]\cdot H_2O$	298	2.00	2.01	1.98	45–80
$[V(NO)_2(CN)_2(phen)]\cdot H_2O$	80	1.99	2.00	1.96	40–80

[a] For spin paired d^5 systems $g_\perp > 2$ and $g_\parallel < 2$; see ref. 22. [b] The available data so far obtained for spin paired d^5 systems do not permit an unequivocal assessment of $\langle A_\perp\rangle_V$, $\langle A_\parallel\rangle_V$ and $\langle A_0\rangle_V$.

because it contains KCl impurity. The two L–L derivatives (II and III) show interesting EPR signals (see Fig. 1) for polycrystalline samples at room temperature and 80 K. The single line (for details see Table 1) in both cases is superimposed on an octet arising from coupling to the spin-active ^{51}V nucleus ($I = 7/2$). The spectrum of complex I is comparable with that of II and III. The absence of ^{51}V–^{15}N or ^{51}V–^{13}C super hyperfine splitting indicates that the unpaired electron is essentially localised in a predominantly metal orbital (here b_2 orbital; see below).

As with $\{M(NO)\}^6$ systems, it may be assumed that in these $\{M(NO)_2\}^5$ species the two nitrosyl groups in *cis*-position should deviate only very slightly from linearity because of the nature of HOMO in this type of system [20]. However, the electronic configuration in the ion $[V(NO)_2(CN)_4]^{2-}$ (the field created by its symmetry species being not assumed to differ much from that of C_{2v}) may be $(a_2)^2(a_1)^2(b_2)^1$. Consequently, the four observed electronic transitions may be designated [19] as $b_2 \to a_1$, $b_2 \to b_1$, $b_2 \to b_2$ and $b_2 \to a_1$ in order of increasing energy. On the other hand, the molecular symmetry species of the L–L derivatives should not be higher than C_s, and hence, the four observed EAS bands may be due to $a' \to a'$, $a' \to b'$, $a' \to a'$ and $a' \to a'$ transitions [19]. It is pertinent to mention here that the $\{V(NO)_2\}^5$ moiety reported here is the second known odd electron dinitrosylmetal species, the first being $\{Re(NO)_2\}^7$ [20].

Experimental

Preparation of $K_2[V(NO)_2(CN)_4] \cdot xH_2O$ (I)

A solution of ammonium metavanadate (1.0 g; 8.5 mmol) in water (50 ml) containing KOH (6 g, 107 mmol) was treated with an excess of solid KCN (8 g, 123 mmol). The solution was then filtered and $NH_2OH \cdot HCl$ (8.8 g, 127 mmol) was added. The orange solution obtained was heated to boiling for 2 h with continuous stirring until no more ammonia was evolved, extra water being added at intervals to maintain the total volume of the solution at 50 ml. The dark red solution obtained was cooled to 0°C, filtered, and then slowly added to chilled ethanol. An orange solid separated out, and the supernatant liquid was carefully decanted off and the solid was dissolved in a minimum volume of water (10 ml) then reprecipitated with chilled ethanol. The process was repeated 3–4 times and the bright orange solid was finally filtered off, washed with chilled ethanol and ether, and dried in vacuo over fused $CaCl_2$. It contained a small amount of KCl impurity and so the C, H, N and V analyses were low. Yield 1.5 g. IR: (ν(CN) 2090(s), 2050(sh); (ν(NO)) 1650(s), 1520(s); (ν(VN)(NO)) 590(w); (ν(VC) 535(m); δ(VNO) 520(w); δ(VCN) 300(w) cm^{-1}; λ_{max} (in H_2O): 720, 460, 400(sh) and 260 nm.

Preparation of $[V(NO)_2(CN)_2(L\text{–}L)] \cdot H_2O$ (II and III)

A solution of the above orange solid (1.0 g) in 50 ml water was heated to 80°C and an aqueous (50 ml) solution of L–L (1.0 g; 6.4 mmol for bipy and 5.5 mmol for phen) was added with stirring. The orange red precipitate was filtered off, washed with water, dried in vacuo, then washed thoroughly with benzene and dried under reduced pressure. The products are soluble in CH_3CN. Yields 1.8 g (60% based on VO_4^{3-} initially taken) for II and 2.0 g, (60%) for III. Anal. Compound II. Found: C, 42.4; H, 3.1; N, 24.6; V, 14.9; H_2O (DTA (exothermic) and TGA), 5.4; Mol. wt. (CH_3CN, osmometric), 310. $C_{12}H_{10}N_6O_3V$ calcd.: C, 42.7; H, 2.9; N, 24.9; V, 15.1,

H_2O, 5.3%; mol. wt. 337. Compound III. Found: C, 46.3; H, 3.1; N, 22.8; V, 13.9; H_2O 5.2; Mol. wt. (CH_3CN), 340. $C_{14}H_{10}N_6O_3V$ calcd.: C, 46.5; H, 2.8; N, 23.2; V, 14.1; H_2O, 5.0%. Mol. wt. 361. IR: (ν(CN)) 2120(m), 2090(sh); (ν(NO)) 1680(s), 1540(s); (ν(VN)(NO)) 640(w,b); in both II and III. Also, (ν(VC)(CN)) 410(w); (ν(VN)(bipy)) 345(vw) in II; (ν(VC)(CN)) 420(w) and (ν(VN)(phen)) 340(vw) cm^{-1} in III (for the authenticity of the assignment of the IR bands see ref. 21); λ_{max} (in CH_3CN): 750 (ϵ_{max} 20 l mol^{-1} cm^{-1}), 490 (1600), 410 (850) and 300 (8410) for II and 725 (15), 480 (225), 420 (175) and 270 (3390) nm for III.

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