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LETTER

Isolation and characterisation of dinitrosyl complexes of vanadium(−I)

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The inception of nitrosyl chemistry started with the isolation of nitroprusside in 1849. However, the knowledge of nitrosyl chemistry of vanadium [1–6] is very meagre and nothing is known about the bisbipyridinedinitrosylvanadium(−I) cation to date. The starting compound for the preparation of the complexes has the $\{VNO\}^4$ moiety which is changed into the $\{V(NO)_2\}^6$ moiety, a unique feature. This paper also presents the first decomposition and hydrolysis study of the nitrosyl complex by infrared spectra.

Experimental

One gram of $K_3[V(CN)_5(NO)]\cdot 2H_2O$ and 1.7 g of bipyridine (1:4 mole ratio) were dissolved in 40 ml of deaerated water. The container was attached with a vaccum pump until boiling started. Then it was closed with a standard joint and left for 24 h with occasional stirring; during this time a red complex was separated. This was filtered off quickly under suction, repeatedly washed with an aqueous solution of NaCN and finally with water. The compound was dissolved in methanol and reprecipitated with ether twice to free the product from any unreacted bipyridine. Finally, the product $[V(NO)_2(bipy)_2]CN^-$ was washed with ether and dried *in vacuo* over P_2O_5 (yield ~0.35 g). *Anal.* Found: C, 56.3; H, 3.8; N, 20.4; V, 10.8. Calc.: C, 56.1; H, 3.5; N, 21.8; V, 11.3%.

$[V(NO)_2(bipy)_2]ClO_4$ was prepared by dissolving 0.2 g of freshly prepared $[V(NO)_2(bipy)_2]CN$ in 10 ml of methanol and to this an aqueous solution (10 ml) of $NaClO_4$ (0.5 g) was added. Further dilution was affected by adding 100–150 ml of water. The turbid solution was allowed to settle in a closed container and the red precipitate thus obtained was filtered under suction, washed twice with water and dried *in vacuo* over P_2O_5 (yield ~0.22 g). *Anal.* Found: C, 45.6; Cl, 6.8; H, 3.2; N, 15.7; V, 9.9. Calc.: C, 45.9; Cl, 6.7; H, 3.0; N, 16.0; V, 9.7%.

Results and discussion

The cyanide salt is a deep red solid, moderately soluble in water and freely soluble in methanol to impart a deep red colour. The compound is only stable when it is kept over P_2O_5 in the solid state. Its IR spectrum (Table 1) shows two very strong nitrosyl stretching bands at 1675 and 1538 cm^{-1} characteristic of *cis*-$\{V(NO)_2\}$ [7], a strong band at 2118 cm^{-1} assigned to νCN and several bands in the 1600–720 cm^{-1} range due to bipyridine. The compound immediately decomposes in acid solution but is comparatively stable in alkaline medium where on boiling or on keeping it decomposes with the fading of colour and expulsion or bipyridine and change of NO^+ to NO_2^- (Griess's reagent test). After overnight exposure in the laboratory atmosphere the red compound turned into a yellow compound which does not contain any NO^+ or CN^-. The immediate expulsion of hydrocyanic acid suggests that the cyanide salt first hydrolyses and the intermediate hydroxide thus formed starts to decompose.

The corresponding perchlorate salt is more stable in the solid state, is insoluble in water and in nonpolar organic solvents. In alcohols and acetones it is highly soluble. It behaves as a uni-univalent electrolyte in methanol ($\mu = 83.4$ ohm^{-1} cm^2 at 1×10^{-3} M concentration) and is diamagnetic at room temperature. It exhibited very strong IR spectral bands at 1692 and 1546 cm^{-1} characteristic of νNO, a broad and strong band at 1105 cm^{-1} assigned to perchlorate.

The decomposition of $[V(NO)_2(bipy)_2]CN$ (Table 2) has been studied by monitoring the reaction products or the gradual changes occurring during exposure to air by infrared spectroscopy at different time intervals which clearly suggests that the first reaction is a hydrolysis reaction.

$$[V(NO)_2(bipy)_2]CN + H_2O \longrightarrow [V(NO)_2(bipy)_2]OH + HCN$$

The reaction observed is completed within 3 h in contact with air on a well spread sample and the yield is ~80%. By this time νCN completely disappears and a strong band of νOH appears at 3490 cm^{-1}. The corresponding hydroxide salt (yield

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TABLE 1. Infrared spectral data for the $[V(NO)_2]^+$ derivatives

Compound	ν(NO)	Organic ligand vibration (cm^{-1})	Others (cm^{-1})	ν(VN) (cm^{-1})	δ(VNO) (cm^{-1})
$[V(bipy)_2(NO)_2]ClO_4$	1692(vs), 1546(vs)	1600(m), 1490(sh), 1467(m), 1438(m), 1312(m), 1280(w), 1238(w), 1017(w), 967(w), 892(w), 850(w), 755(vs), 730(m)	1105(s,br), 652(m)	636(w), 628(w)	555(w), 496(w)
$[V(bipy)_2(NO)_2]CN$	1675(vs), 1538(vs)	1600(w), 1484(sh), 1464(m), 1438(m), 1313(m), 1275(w), 1238(w), 1224(w), 1163(w), 1150(w), 1100(w), 1059(w), 1046(w), 1021(w), 959(w), 884(w), 850(w), 750(vs), 720(m)	2117(w), 2092(w)	650(w), 634(w)	550(w), 500(w)
$[V(NO)_2(phen)_2]ClO_4$	1695(vs), 1547(vs)	1596(m), 1467(w), 1430(m), 1384(w), 1344(w), 1280(w), 1234(w), 1021(w), 867(m), 840(s), 717(s), 709(sh), 685(w)	1102(s,br), 650(m)	625(w), 619(w)	567(w), 517(w)
$[V(NO)_2(phen)_2]CN$	1693(vs), 1545(vs)	1600(m), 1463(w), 1439(m), 1388(w), 1350(w), 1282(w), 1230(w), 1200(w), 1138(w), 1100(w), 1060(w), 1038(w), 1022(w), 867(m), 846(s), 709(s), 675(w)	2118(w)	642(w), 630(w)	559(w), 496(w)

TABLE 2. Decomposition of $[V(bipy)_2(NO)_2]CN$ as monitored by infrared spectra

Exposure time (h)	ν(CN) (cm^{-1})	ν(NO) (cm^{-1})	ν(OH) (cm^{-1})
0	2118(m), 2154(m)	1671(vs), 1540(vs)	
2	2165(w)	1675(vs), 1542(vs)	3460(m,br)
3		1667(vs), 1538(vs)	3490(s,br)
6		1692(m), 1545(m)	3500(s,br)

~75%) is also obtained via an anion exchange resin (Amberlite IRA-400) from a solution of the perchlorate salt in 50% aqueous alcohol. *Anal.* Found: C, 55.0; H, 4.1; N, 19.5; V, 11.8. Calc.: C, 54.7; H, 3.8; N, 19.0; V, 11.5%. The analysis corresponds to the formula $[V(NO)_2(bipy)_2]OH$. Once the hydroxide is formed the stability is impaired and a sample exposed for 6 h shows decomposition. The reduction in the band profile of the nitrosyl stretching is accompanied by the appearance of a strong and broad band around 1000 cm^{-1} suggesting that some oxo–hydroxo species are formed.

The corresponding phenanthroline analogues behave similarly (Table 1).

The above preparation may be treated as a disproportionation reaction:

$$K_3[V(CN)_5NO]\cdot 2H_2O + \text{bipy(excess)} \longrightarrow$$
$$[V(NO)_2(\text{bipy})_2]CN + V^{II} + V^{III} \text{ complexes}$$

The above reaction where a d^4 configuration changes to a d^6 configuration is parallel to the formation of some zerovalent chromium complexes starting from bivalent compounds [8].

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