Preparation, Fluxional Behaviour, and Decomposition of Bis(cyclopentadienyl)iodonitrosylvanadium. X-Ray Crystal Structure of [(cpVI)₂{cpV(NO)}₂(μ-O)₄]

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$cp_2VX(NO)$ ($cp = C_5H_5$, $X = Br$, I) are fluxional molecules in which linear and bent VNO groups interconvert; the molecule with the linear VNO group necessarily contains at least one ring with less than η^5-hapticity, while $cp_2VI(NO)$ decomposes *in vacuo* in tetrahydrofuran solution to give $[(cpVI)_2\{cpV(NO)\}_2(\mu\text{-}O)_4]$ whose X-ray crystal structure is reported.

The reaction of cp_2VX ($cp = C_5H_5$, $X = Br$, I) with NO in toluene gives two products, both of which analyse as cp_2-VXNO. One is a brown insoluble solid having only weak absorption bands in the region of the i.r. spectrum where $\nu(NO)$ vibrations are expected; I^- can be removed from brown 'cp_2VINO' by washing with water. We believe this form of cp_2VXNO to be a polymer containing $N_2O_2{}^{2-}$ bridges, as postulated previously for 'cp_2TiNO'.[1]

The second cp_2VXNO products are green complexes, soluble in tetrahydrofuran (THF) in which solvent they are monomeric. The iodo-derivative shows *two* sharp $\nu(NO)$ stretching frequencies in both the solid state (1690, 1590 cm⁻¹) and in THF solution (1688, 1580 cm⁻¹). In solution at room temperature the intensity ratio of these bands is approximately 2:1 in favour of the 1580 cm⁻¹ band; in the solid state the ratio is approximately 2.6:1. When $cp_2VI(NO)$ is dissolved in THF, cooled to $-70\,°C$ and precipitated at this temperature by addition of hexane the intensity ratio of the absorption bands of the solid (measured at 20 °C) changes to 6.3:1 in favour of the 1590 cm⁻¹ band. On dissolution and reprecipitation at 20 °C the 2.6:1 intensity ratio is observed once again. At $+60\,°C$ the e.s.r. spectrum (THF solution) shows an almost symmetrical eight-line spectrum typical of a monomeric $cp_2V(X)(Y)$ complex having one unpaired electron. At 20 °C the spectrum shows 16 lines of unequal intensity and on cooling to $-80\,°C$ one set of eight lines increases in intensity at the expense of the other. The less intense set does not disappear before freezing of the solution. The changes in the e.s.r. spectrum are reversible, though at high temperature other irreversible changes slowly occur (*vide infra*).
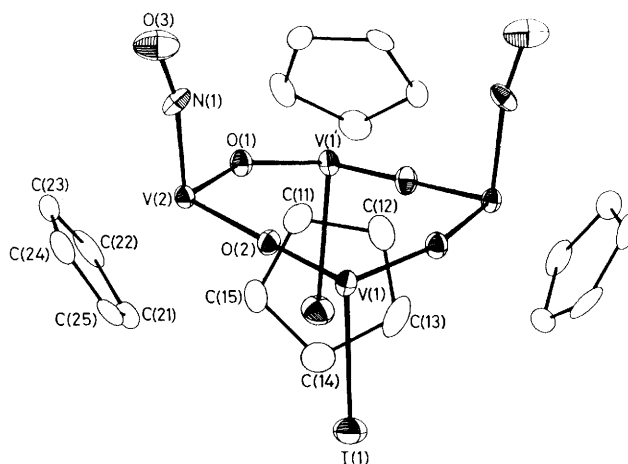

Figure 1. The structure of $[(cpVI)_2\{cpV(NO)\}_2\,(\mu\text{-}O)_4]$.

The only explanation for the above observations is an equilibrium between $cp_2VI(NO)$ having a linear VNO group [$\nu(NO)$ 1690 cm⁻¹] and $cp_2VI(NO)$ having a bent one [$\nu(NO)$ 1590 cm⁻¹],† of which the species with the bent VNO group is the lower energy form since it is present to a greater extent

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† Other examples of linear–bent MNO equilibria are known; see C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304, and M. W. Schoonover, E. C. Baker, and R. Eisenberg, *J. Am. Chem. Soc.*, 1979, **101**, 1880.

at low temperature.‡ The $cp_2VI(NO)$ complex with the bent VNO group is *formally* a 17 electron species with normal η^5-C_5H_5 rings. However the $cp_2VI(NO)$ species with the linear VNO group is *formally* a 19 electron species and like the *formally* 20 electron $cp_2MoI(NO)^2$ species must have abnormal cp ring bonding. In the solid state $cp_2MoI(NO)$ has two planar η^4-C_5H_5 rings;[2] on the other hand $cp_2W(CO)_2$ (also *formally* 20 electrons) has one markedly non-planar η^3-C_5H_5 ring and one η^5-ring.[3] There has been much discussion of the changes in the rings and the MoNO group in $cp_2MoI(NO)$.§ We have not been able to obtain a crystalline sample of cp_2VI-(NO) containing only one form of the molecule.

When set aside in THF under vacuum at room temperature the green monomeric $cp_2VI(NO)$ deposits golden brown crystals over a period of several days. The product of the transformation is the remarkable nitrosyl-oxo-complex $[(cpVI)_2\{cpV(NO)\}_2(\mu\text{-}O)_4]$ as determined by X-ray crystallography (see Figure 1), spectroscopy, and analysis. The VNO groups have angles of 166.9(8)° and the 8-membered ring deviates from planarity in being folded by 20° along the $cpV(1)I$–$cpV(1')I$ axis. The V–O–V angles are 148.1(3) and 179.3(3)°. The mechanism of the transformation of $cp_2VI(NO)$ into $[(cpVI)_2\{cpV(NO)\}_2(\mu\text{-}O)_4]$, which is undoubtedly trig-

gered by the fluxional nature of $cp_2VI(NO)$, is under investigation.

Preliminary results indicate that $[cp_2VBr(NO)]$ behaves similarly to $[cp_2VI(NO)]$ [$\nu(NO)$ 1660, 1550 cm^{-1} in the solid state] except that on precipitation at -30 °C only the low frequency i.r. band was observed. Addition of NO to cp_2VCl gave a material with several $\nu(NO)$ absorption bands in the i.r. spectrum and gaseous N_2O was also observed. It appeared that partial oxidation of cp_2VCl occurred, as was found for cp_2TiCl.[1]

Crystal data: $C_{20}H_{20}I_2N_2O_6V_4$, $M = 842.0$, monoclinic, $C2/c$, $a = 18.358(3)$, $b = 8.152(1)$, $c = 17.590(2)$ Å, $\beta = 91.27(2)°$, $Z = 4$, $R = 0.030$, $R_w = 0.052$ for 1304 observed reflections with $2\theta < 45°$ (measured on a Picker FACS-1 diffractometer) and 195 variables.¶

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‡ The possibility that the observed i.r. absorption bands are due to the equilibrium $cp_2VI(NO) \rightleftharpoons [cp_2V(NO)]^+ + I^-$ can be discounted because $[cp_2V(NO)]^+$ can be obtained independently from the reaction between $cp_2V(CO)$ and NO^+, and shows one absorption at 1555 cm^{-1}.

§ A linear–bent MoNO transformation has been postulated as occurring as a mechanistic intermediate in the fluxional behaviour of $cp_2Mo(R)(NO)$ complexes (F. A. Cotton, in 'Dynamic Nuclear Magnetic Resonance Spectroscopy,' eds. F. A. Cotton and L. M. Jackman, Academic Press, New York, 1975). On the other hand a process involving an η^3-C_5H_5 ring and a rigid linear MoNO group has also been proposed (M. M. Hunt, W. G. Kita, B. E. Mann, and J. A. McCleverty, *J. Chem. Soc., Dalton Trans.*, 1978, 467).

References

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2 F. A. Cotton and P. Legzdins, *J. Am. Chem. Soc.*, 1968, **90**, 6232; J. L. Calderon, F. A. Cotton, and P. Legzdins, *ibid.*, 1969, **91**, 2528; F. A. Cotton and G. A. Rusholme, *ibid.*, 1972, **94**, 402.
3 G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer, *J. Organomet. Chem.*, 1978, **145**, 529.

¶ The atomic co-ordinates for this work are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.