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# Oxovanadium(V)-meso-tetraphenylporphine

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Vanadium, embedded in porphine systems, is an integral part of many fossils such as crude oil [1]. The vanadium porphines, which contain the $VO^{2+}$ ion, are thought to be secondary products formed during fossilization from unspecified vanadium compounds and metal porphines (*via* transmetallation) or their precursors.

The biological role of vanadium in living plant and animal tissues has only very recently been fully recognized (see [2] to [5] for reviews). An as yet unspecified complex vanadium compound containing the main part of the vanadium in the oxidation state +III has been identified in so-called vanadocytes in the circulatory system of several tunicates [3, 6] and might have the function of storage of redox equivalents. The inhibitory effect of vanadate(V) towards nucleases, phosphatases and ATPases is now well established; the inhibition of ATPase ceases as vanadate(V) is reduced physiologically to oxovanadium(IV). There appears to be evidence that the vanadyl ion is then bound to hemoglobin [7]. The essential role of vanadium in the photosynthetic apparatus has also been demonstrated [8].

The paramagnetic $VO^{2+}$ porphines have been extensively studied by ESR spectroscopy [9]. The prospect of obtaining complementary $^{51}V$ NMR information on diamagnetic $VO^{3+}$ species prompted us to attempt the preparation of oxovanadium(V) porphines. In order to establish a chart of vanadium chemical shifts, $\delta(^{51}V)$, which can be employed as a diagnostic tool for structure assignments, we also present as yet unpublished $^{51}V$ NMR data on vanadium(V) compounds containing vanadium-nitrogen bonds, together with comparative data on selected compounds from the literature (Table I).

There are only a few reports on vanadium(V)–nitrogen systems related to our present study. These include $VOCl_2(NR_2)NHR_2$ [18], $VO(OiPr)_{3-n}(NEt_2)_n$ [19] and $VOCl_3(NEt_3)_2$ [20], and a somewhat dubious $^{51}V$ NMR investigation of reaction products obtained from, *e.g.* $VOCl_3$ and diethylamine in acetonitrile [21]. It has been noted that the $VO^{3+}$ ion is too small to coordinate to the porphine frame in the manner commonly observed with transition metal ions (including $VO^{2+}$) [22]; other coordination modes should be possible, though.

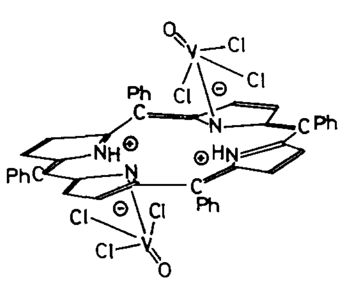

Fig. 1. Possible structure of $[(TPPH_2)^{2+}(VOCl_3^-)_2]$ (*1*), based on analytical and spectroscopic (UV, IR, $^{51}V$ NMR) characteristics. For the $\{VOCl_3NR_2^-\}$ moiety, tetragonal geometry as in $[VOCl_4]^-$ [24] and $[VOBr_4]^-$ [25] is presumed.

We have now successfully prepared an oxovanadium(V) porphine from $VOCl_3$ and meso-tetraphenylporphine ($H_2TPP$) which, to our knowledge is the first diamagnetic vanadium porphine. A structure based on analytical and spectroscopic data is shown in Fig. 1. The complex may be considered an internal salt containing the $[VOCl_3(NR_2)]^-$ moiety and the diprotonated tetraphenylporphine cation, hence $[(TPPH_2)^{2+}(VOCl_3^-)_2]$ (*1*).

In a typical experiment, 370 mg $VOCl_3$ (2.14 mmol) dissolved in 40 ml $O_2$-free, absolute $CCl_4$ were added dropwise over 2 h to a stirred solution of 1.0 g (1.62 mmol) $H_2TPP$ in 200 ml $CCl_4$ kept under $N_2$. The formerly dark-red solution turned to a deep green and gradually, a green powder precipitated. The mixture was stirred at room temperature for an additional 10 h, while a weak $N_2$ stream was passed through the solution. The precipitate was filtered off ($N_2$ atmosphere) and washed with $CCl_4$ to remove unreacted $H_2TPP$ until the filtrate was colourless. The residue was then dried for five hours under high vacuum to yield 730 mg (70% relative to $VOCl_3$) of an emerald green, powdery product, which was stored under $N_2$. Analysis: $C_{44}H_{30}Cl_6N_4O_2V_2$ (M = 961.4) calcd. C, 54.97; H, 3.15; Cl, 22.12; N, 5.83; V, 10.60. Found C, 55.3; H, 3.45; Cl, 20.9; N, 6.00; V, 10.0%.

In iPrOH, the complex degrades to form $VO(OiPr)_3$ and $[H_4TPP]^{2+}$. This alcoholysis is quite generally observed with $V{-}NR_2$ and $V{-}Cl$ bonds. In $CH_3CN$, $VO(NR_2)_3$ is obtained. With water/acetone, $H_2TPP$ is recovered and an acidic solution (pH *ca.* 2) containing the $VO_2^+$ ion is formed. All these reactions are indicated by the $^{51}V$ NMR spectra (Table I). Stable, dark-green solutions are obtained with $CHCl_3$, and these were used for spectroscopic investigations.

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TABLE I. $^{51}V$ Chemical Shifts of Vanadyl Porphines and Related Compounds.

| System[a] | Medium | Assignment[c] | $\delta(^{51}V)$[b] (ppm) | Ref. |
|---|---|---|---|---|
| $VOCl_3/H_2TPP$ | $CHCl_3$ | $[(TPPH_2)^{2+}(VOCl_3^-)_2]$ | −481 | d |
| | $CH_3CN$ | $VO(NR_2)_3$ | −370 | d |
| | iPrOH | $VO(OiPr)_3$ | −629 | d |
| | $H_2O$/acetone | $[VO_2]^+$ | −540 | d |
| $VOCl_{3-n}(OR)_n$[e]$/H_2TPP$ | $CHCl_3$ | | −481 | d |
| $VOF_3/H_2TPP$ | $CHCl_3$ | $[(TPPH_2)^{2+}(VOF_3^-)_2]$ | −626 | d |
| $VOCl_3/H_2OEP$ | $CHCl_3$ | $[(OEPH_2)^{2+}(VOCl_3^-)_2]$ | −497 | d |
| | $CH_3CN$ | $VO(NR_2)_3$ | −377 | d |
| $[pyH][VOCl_4]^-$ | $CH_2Cl_2$ | | −319 | d |
| $[VO_2Cl_2]^-$ | $CH_3CN$ | | −301 | 10 |
| $VO(NEt_2)_3$ | $CH_3CN$ | | −365 | 11 |
| $VOCl_3/NH_2Ph$ | DMF, $KClO_3$[h] | $VO(NHPh)_3$ | −364 | d |
| $VOCl_3$/2-$NH_2py$ | DMF | $VO(NHpy)_3$ | −361 | d |
| | THF, $KClO_3$[h] | $VO(NHpy)_3$ | −372 | d |
| | THF, iPrOH | $VO(NHpy)_3$, $VO(OiPr)_3$ | −361, −623 | d |
| $VOCl_2(NEt_2)$ | neat | | −212 | 14 |
| $[VO_2]^+$ | $H_2O$, pH = 2 | | −541 | 12 |
| $VO(OiPr)_3$ | $Et_2O$ | | −625 | 13 |
| $VO(OiPr)_2NEt_2$ | neat | | −593 (t, 105)[f] | 14 |
| $VO(OiPr)(NEt)_2$ | neat | | −462 | 14 |
| $[VOF_4]^-$ | $CH_3CN$ | $[VOF_4(CH_3CN)]^-$ | −778 | 15 |
| $VOF_3$ | $CHCl_3$ | | −582 | d |
| $[VO_2F_4]^{3-}$ | $H_2O$ | | −775 (q, 117)[g] | 16 |

[a] Abbreviations: $H_2TPP$ = meso-tetraphenylporphine, $H_2OEP$ = octaethylporphine, py = pyridine. [b] At 23.66 MHz (Bruker WH 90) and 300 ± 2 K relative to $VOCl_3$ neat. [c] Some of the assignments are tentative. [d] This work. [e] n = 1, R = nBu; n = 2, R = iPr. [f] 1:1:1 triplet due to $^1J(^{51}V-^{14}N)$ coupling. A similar coupling (J = 95 Hz) has formerly been reported for $(Me_3SiO)_3V{=}NtBu$ [17]. [g] Binominal quintet due to $^1J(^{51}V-^{19}F)$ coupling. [h] Addition of $KClO_3$ was necessary to prevent reduction to $VO^{2+}$.

Spectroscopic characteristics which, apart from the analytical data, lead to the formulation depicted in Fig. 1, are the following: The UV spectrum [354.2 ($\epsilon$ = 0.27), *ca.* 420 (shoulder), 444.7 (1.0), 608.6 (0.10), 660.5 (0.54) nm] is practically identical to that of $[H_4TPP]^{2+}$ [356.5 ($\epsilon$ = 0.076), *ca.* 422 (shoulder), 444.2 (1.0), 606 (weak), 659.6 (0.13) nm]. This is also true for the IR spectrum; the only band in addition to the pattern exhibited by $[H_4TPP]^{2+}$ is a medium absorption at 908 $cm^{-1}$ (KBr) which we attribute to the $\nu$(VO). For $[VOCl_4]^-$, the VO stretch lies at 967 ± 3 [23, 24], for $[VOBr_4]^-$ at 922 $cm^{-1}$ [25]. Further, there are weak bands at 446, 430 and 322 $cm^{-1}$ (CsI), which may correspond with $\nu$(VCl), $\nu$(VN) and deformation modes. The $^{51}V$ NMR shows a comparatively sharp signal (width at half-height 45 ± 20 Hz) at −481 ± 2 ppm (relative to $VOCl_3$). This shift value is in accord with the assumption that one chloro ligand in $[VOCl_4]^-$ ($\delta$ = −319 ppm) is replaced by an amido group of the tetraphenylporphine ligand. Replacement of the first Cl in $VOCl_3$ by $NR_2$ increases the shielding of the $^{51}V$ nucleus by 212 ppm [14]. In $VOCl_2(NEt_2)$, the amido ligand accounts for one fourth of the ligand-induced shielding; in a complex ion $[VOCl_3(NEt_2)]^-$, the contribution of $NEt_2$ to $\delta(^{51}V)$ should only be one fifth of the total shielding, or 80% of −212, *i.e.* – 170 ppm. Adding this value to −319 gives −489 ppm, which is satisfactorily close to the observed $\delta(^{51}V)$ = −481 ppm for the two $\{VOCl_3N\langle\}^-$ moieties in *1*.

We have also investigated the reactions between $H_2TPP$ and $VOCl_2(OnBu)$, $VOCl(OiPr)_2$, $VO(OiPr)_3$ and $VOF_3$, respectively. The tris(ester) did not react. The mixed ester–chlorides reacted to give green compounds with the same spectroscopic characteristics as *1*, including the $\delta(^{51}V)$ values (*cf.* Table I), but substantially lower vanadium contents (6.5%). Vanadyltrifluoride gave an only fairly stable green compound with UV and IR spectra practically identical to those of *1*. However, the vanadium nucleus is more shielded ($\delta$ = −626 ppm) than in 1 and typical for a $\{VOF_3(NR_2)\}^-$ moiety (replacing F by $NR_2$ deshields the $^{51}V$ nucleus). Finally, the reaction between $VOCl_3$ and octaethylporphine yielded a dark-purple product. IR and UV spectra are those of the protonated porphine. $\delta(^{51}V)$ of the red $CHCl_3$ solution is −497 ppm; hence, a complex analogous to *1* is probably formed.

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