BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3007—3011 (1973)

ESR Evidence for the Destruction of the Four-membered Chelate Structure of Bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV) by Pyridine Bases

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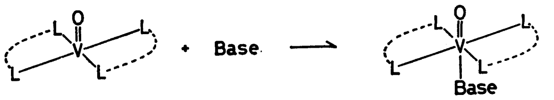
(Received March 31, 1973)

The interaction of bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), $VOdtp_2$, with pyridine bases has been studied in toluene by ESR. It has been found that the four-membered chelate structure of $VOdtp_2$ is disrupted by pyridine bases to form the complex species identified as $VOdtp_2 \cdot Py$ and $VOdtp_2 \cdot Py_2$ by their characteristic ESR spectra. The coordination structures of the newly-formed complexes are discussed in association with the substitution equilibria involved.

It is well known that square pyramidal oxovanadium(IV) complexes coordinated with bidentate ligands form 1 : 1 adducts in solutions with a variety of bases according to this expression:[1]



For example, the base adducts of bisacetylacetonato oxovanadium(IV) have been worked out[2] and the effects of adduct formation on the optical absorption and ESR spectra have also been reported.[3]

We have made an ESR investigation of the reaction of bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV),

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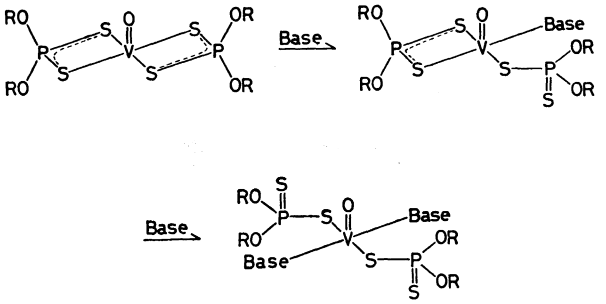
[1] J. Selbin, *Chem. Rev.*, **65**, 153 (1965).

[2] A. Rosenheim and H. Yu Mong, *Z. Anorg. Chem.*, **148**, 34 (1925); M. M. Jones, *J. Amer. Chem. Soc.*, **76**, 5995 (1964); R. T. Claunch, T. W. Martin, and M. M. Jones, *ibid.*, **83**, 1073 (1961); K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, **83**, 4533 (1961); J. Selbin, H. R. Manning, and G. Cessac, *J. Inorg. Nucl. Chem.*, **25**, 1253 (1963).

[3] I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963); J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, **26**, 37 (1964); R. L. Carlin and F. A. Walker, *J. Amer. Chem. Soc.*, **87**, 2128 (1965); F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).

VOdtp$_2$, with pyridine bases. As a result, we found that pyridine bases displace equatorial sulfur ligands, leading to the partial destruction of the four-membered chelate rings, as is indicated below:



In the present report, we wish to describe the evidence for the destruction of the chelate structure, together with the characteristics of this reaction, since no such type of reaction has yet been reported for oxovanadium complexes.

Experimental

Materials. *O,O'*-Diethyldithiophosphoric acid (dtpH) was prepared as has been described previously.[4] Vanadyl sulfate hydrate ($VOSO_4 \cdot nH_2O$) was obtained from the Kishida Kagaku Co. Toluene and pyridine (G.R. Grade, Wako Junyaku Kogyo Co.) were purified by distillation from calcium hydride and potassium hydroxide respectively. All the other reagents used were of a G.R. grade and were also obtained commercially.

*Preparation of Bis(*O,O'*-diethyldithiophosphato)oxovanadium(IV), VOdtp$_2$.* Vanadyl sulfate hydrate was treated with sodium carbonate, and the precipitate was filtered and washed with distilled water until free of sodium sulfate. The precipitate was immediately added to an isopentane solution of dtpH under a flow of dry nitrogen. The suspended mixture was then stirred at room temperature until the precipitate almost dissolved. The resulting purple solution was filtered; the filtrate was then cooled by the rapid evaporation of isopentane with a vigorous flow of nitrogen to separate out a crystalline solid. The repeated recrystallization of the solid from isopentane under an atmosphere of nitrogen gave blue-purple, needle-like crystal. (Anal. Calcd. for $VO[S_2P(OC_2H_5)_2]_2$: C, 21.97; H, 4.61; V, 11.64%. Found: C, 22.12; H, 4.69; V, 11.90%.).

Measurements of the ESR Spectra. Since toluene and pyridine solutions of VOdtp$_2$ were unstable to air, all the measurements were carried out on sample solution carefully prepared in an atmosphere of nitrogen or *in vacuo*. The ESR spectra were recorded both at room temperature and at 77 K with JEOL spectrometers, Model P-10 and ME-1X (X-band), using 100 KHz field modulation. The magnetic field was calibrated with an ESR marker, MgO : Mn^{2+} powder, supplied by JEOL. Powdered DPPH was used as the reference in the determination of the *g*-values.

Results and Discussion

Interpretation of ESR Spectra and Structures of Oxovanadium Complexes in Solutions. Toluene solutions containing VOdtp$_2$ and pyridine bases in various mole ratios, as well as toluene and pyridine solutions of VOdtp$_2$, were subjected to ESR measurements both at room temperature and at 77 K. Typical ESR spectra thus obtained are illustrated in Figs. 1 and 2, while the ESR parameters calculated by the method of Kivelson and Lee[5] are presented in Table 1.

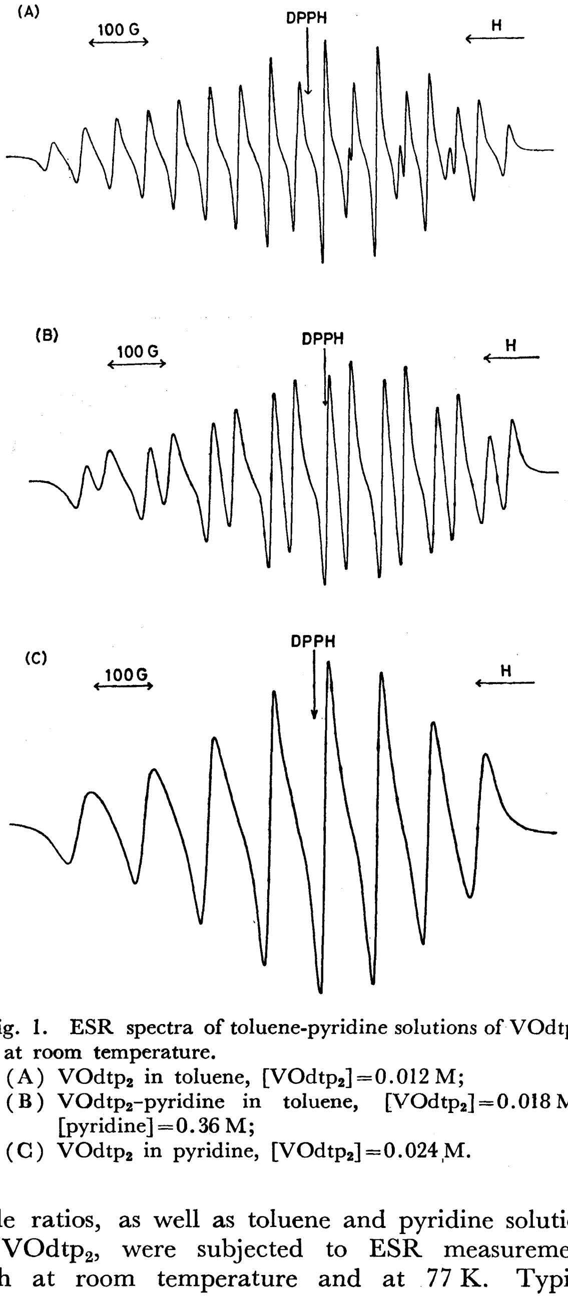


Fig. 1. ESR spectra of toluene-pyridine solutions of VOdtp$_2$ at room temperature.
(A) VOdtp$_2$ in toluene, $[VOdtp_2]=0.012$ M;
(B) VOdtp$_2$-pyridine in toluene, $[VOdtp_2]=0.018$ M, $[\text{pyridine}]=0.36$ M;
(C) VOdtp$_2$ in pyridine, $[VOdtp_2]=0.024$ M.

VOdtp$_2$ in Toluene Solution: As is illustrated in Figs. 1–A and 2–A, a toluene solution of VOdtp$_2$ gave spectra quite similar to those previously reported[6,7] for VOdtp$_2$ in non-coordinating solvents. It can be seen from Figs. 1–A and 2–A that eight hf lines characteristic of the

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[4] M. Sato, M. Yanagita, Y. Fujita, and T. Kwan, This Bulletin, **44**, 1423 (1971).

[5] D. Kivelson and S. K. Lee, *J. Chem. Phys.*, **41**, 1896 (1964).

[6] N. S. Garif'yanov and B. M. Kozyrev, *Teor. Eksp. Khim.*, **1**, 525 (1965); N. S. Garif'yanov, B. M. Kozyrev, and I. F. Gainnulin, *Zh. Strukt. Khim.*, **9**, 529 (1968); I. V. Obchinnikov, I. F. Gainnulin, N. S. Garif'yanov, and B. M. Kozyrev, *Dokl. Akad. Nauk SSSR*, **191**, 395 (1970); R. G. Cavell, E. D. Day, W. Byers, and P. M. Watkins, *Inorg. Chem.*, **11**, 1591 (1972).

[7] J. R. Wasson, *ibid.*, **10**, 1531 (1971); M. Sato, M. Yanagita, Y. Fujita, and T. Kwan, Preprints of 10th Electron Spin Resonance Symp. Japan, Osaka (1971), p. 59.

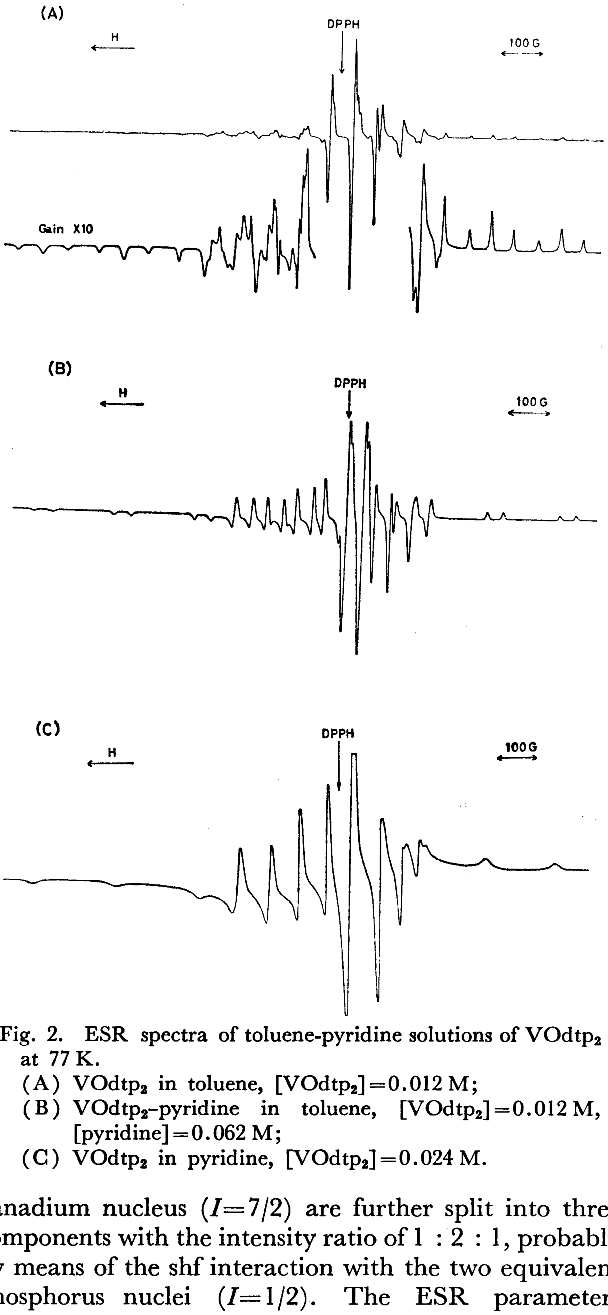
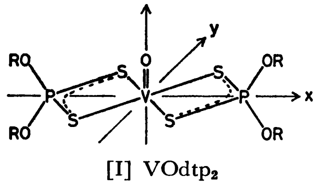


Fig. 2. ESR spectra of toluene-pyridine solutions of $VOdtp_2$ at 77 K.
(A) $VOdtp_2$ in toluene, $[VOdtp_2]=0.012$ M;
(B) $VOdtp_2$-pyridine in toluene, $[VOdtp_2]=0.012$ M, $[pyridine]=0.062$ M;
(C) $VOdtp_2$ in pyridine, $[VOdtp_2]=0.024$ M.

vanadium nucleus ($I=7/2$) are further split into three components with the intensity ratio of 1 : 2 : 1, probably by means of the shf interaction with the two equivalent phosphorus nuclei ($I=1/2$). The ESR parameters (Table 1) are in good agreement with those obtained by previous workers.[6,7]

On the other hand, it has already been suggested[6,7] that $VOdtp_2$ has a tetragonal pyramidal structure which can be depicted as:



[I] $VOdtp_2$

Such a structural model seems to be quite reasonable, since this is the basic type of coordination known for many oxovanadium(IV) complexes[8] and since dithiophosphate ligands have, in general, a great tendency to form a four-membered chelate structure with metal ions.

Furthermore, the suggested structure [I], which possesses a local symmetry of C_{2v},[9] can well satisfy the ESR parameters shown in Table 1. The g-values and vanadium hf constants are in good agreement with the theory that assumes a single unpaired electron located in an A_1 orbital mainly consisting of the vanadium $3d_{x^2-y^2}$ orbital.[5,10] The isotropic phosphorus constant ($a^{P}=51$ Gauss) can also be interpreted in terms of a direct vanadium($3d_{x^2-y^2}$)– phosphorus(3S) interaction.[7] It is important for us to note that the vanadium $3d_{x^2-y^2}$ orbital possesses the correct symmetry so as to interact directly with the two equivalent phosphorus 3s orbitals.

Our interpretation of the ESR spectra of $VOdtp_2$ in toluene is, in fact, in good agreement with those given by the previous workers and can be taken to furnish further support for the proposed structure [I]. We have, however, noted that such a structure is valid only when $VOdtp_2$ is present in non-coordinating solvents.[11]

$VOdtp_2$-Pyridine Bases in Toluene Solutions: When a certain amount of pyridine bases, such as pyridine, 4-methylpyridine, and 4-cyanopyridine, was added to a toluene solution of $VOdtp_2$, the spectra shown in Figs. 1–A and 2–A were replaced by the spectra characterized by 16 resonance lines. Typical examples are illustrated in Figs. 1–B and 2–B. It seems to us that such spectra are quite a new type of spectra. However, these spectra can easily be explained if the shf interaction due to one phosphorus nucleus split each of the eight vanadium hf lines into two components equal in intensity. In accordance with this assumption, the liquid solution spectrum (Fig. 1–B) consists of 16 resonance lines, while the frozen solution spectrum (Fig. 2–B) consists of two sets of 16 resonance lines, corresponding to the parallel and perpendicular directions ($g_{\parallel}$ and $g_{\perp}$).

The intensity of the 16-line spectrum was examined at room temperature as a function of the concentrations of the pyridine bases. The intensities of the 16-line spectrum relative to the 24-line spectrum[12] were found to be strongly dependent upon the mole ratios of the pyridine bases to $VOdtp_2$ in solutions. For example, the gradual addition of pyridine to a toluene solution of $VOdtp_2$ brought about a progressive decrease in the intensity of the 24-line spectrum, accompanied by a simultaneous appearance of the 16-line spectrum; the superimposed spectra of the 16- and 24-line spectra with comparable intensities were observ-

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[8] R. J. Clark, "The Chemistry of Titanium and Vanadium," Elsevier Publishing Co., New York (1968), p. 202.

[9] The ligand field can be considered as a strong C_{4v} component with a perturbation lowering the symmetry to C_{2v}.

[10] B. R. McGarvey, *Transition Metal Chemistry*, **3**, 89 (1966).

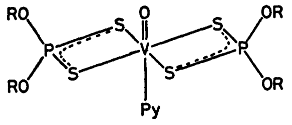
[11] We have been unable to observe such spectra as are shown in Figs. 1-A and 2-A for $VOdtp_2$ dissolved in coordinating solvents, such as methyl alcohol, ethyl alcohol, diethylether, and tetrahydrofuran. This indicates that $VOdtp_2$ is highly reactive toward the coordinating solvents to be converted into another complex species. Further study along this line is now in progress.

[12] The spectrum shown in Fig. 1–A is conveniently denoted as the "24-line spectrum," although fewer than the 24 expected lines are resolved because of line overlappings.

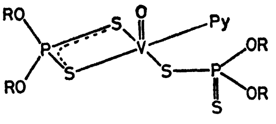
ed when the mole ratio of [pyridine]/[$VOdtp_2$] was around 2; the 24-line spectrum completely disappeared to give such a typical 16-line spectrum as is shown in Fig. 1–B when the [pyridine]/[$VOdtp_2$] ratio reached more than 10. A further increase in the [pyridine]/[$VOdtp_2$] ratio beyond 100, however, caused a decrease in the intensity of the 16-line spectrum, with an appearance of the 8-line spectrum, as will be described below.

On the other hand, Job's method of continuous variations, as applied to the $VOdtp_2$–pyridine base system at room temperature, showed that the intensity of the 16-line spectrum reached a maximum at about 50 mol% of the pyridine base. It is thus evident that one mole of $VOdtp_2$ reacts with one mole of the pyridine base to form a complex species, which then gives rise to the 16-line spectrum. It seems, therefore, probable that the complex species may result either from the addition of the pyridine base to the open coordination position of $VOdtp_2$ or from the displacement of the sulfur ligand by the pyridine base, and that the complex species may have a stoichiometry of $VOdtp_2 \cdot Py$, where Py denotes the pyridine base.

On the basis of the above considerations, we can now discuss the following structural models:



[II] $VOdtp_2 \cdot Py$



[III] $VOdtp_2 \cdot Py$

where it is assumed that the pyridine base in [II] is weakly coordinated as the sixth ligand, while the pyridine base in [III] is rather strongly coordinated as an equatorial ligand and the sulfur ligand displaced by the pyridine base is free or weakly coordinated to the axial site *trans* to the oxygen atom.

Both of the presumed models are compatible with the *g*-values and vanadium hf constants obtained (Table 1), if these structures are taken to have an approximate symmetry of C_{2v} with the electronic ground state of $^2A_1$, having an unpaired electron mainly in the vanadium $3d_{x^2-y^2}$ orbital, as in the case of $VOdtp_2$[I].

However, the observed shf splitting due to one phosphorus nucleus is in accord with the [III] structure rather than the [II] structure, because it can be expected from [II] that the two phosphorus nuclei take part in the shf interaction equivalently. On the other hand, one can reasonably expect from [III] that only the phosphorus nucleus located in the direction of the lobes of the vanadium $3d_{x^2-y^2}$ orbital contributes to the shf splitting, while the other phosphorus nucleus does not give rise to the resolved shf splitting because of its situation removed from interaction with the vanadium $3d_{x^2-y^2}$ orbital.

It is interesting to note that the isotropic shf constant ($a^P=37$ Gauss) for $VOdtp_2 \cdot Py$[III] is decreased considerably as compared with that ($a^P=51$ Gauss) found for $VOdtp_2$ [I]. This implies that the extent of the delocalization of the unpaired electron over the phosphorus 3s orbital is reduced from 1.4% for $VOdtp_2$ to 1.0% for $VOdtp_2 \cdot Py$.[13] Such a reduction may be explained on the assumption that either the lowering of the structural symmetry or the weakening of the four-membered chelate structure caused by the introduction of the pyridine base in the square plane results in the reduction of a direct vanadium($3d_{x^2-y^2}$)-phosphorus(3s) interaction.

TABLE 1. ESR PARAMETERS FOR $VOdtp_2$ DISSOLVED IN TOLUENE-PYRIDINE SOLUTIONS[a]

Solvents	Toluene	Toluene-Pyridine[b]	Pyridine
Typical spectra assignment	Figs. 1-A, 2-A	Figs. 1-B, 2-B	Figs. 1-C, 2-C
	$VOdtp_2$[I]	$VOdtp_2 \cdot Py$[III]	$VOdtp_2 \cdot Py_2$[IV]
Isotropic values			
g_0	1.981	1.976	1.974
$\lvert a^V \rvert$ Gauss	95.5	95.5	96.0
$\lvert a^P \rvert$ Gauss	51.0(2P)[c]	37.0(1P)[c]	—[d]
Anisotropic values			
$g_\parallel$	1.967	1.958	1.955
$g_\perp$	1.987	1.982	1.980
$\lvert A^V_\parallel \rvert$ Gauss	168	170	171
$\lvert A^V_\perp \rvert$ Gauss	59	59	59
$\lvert A^P_\parallel \rvert$ Gauss	52(2P)	37(1P)	—
$\lvert A^P_\perp \rvert$ Gauss	50(2P)	38(1P)	—

a) Isotropic and anisotropic values, obtained from the liquid solution spectra (Fig. 1) and the frozen solution spectra (Fig. 2) respectively, are presented. It is noted that all the experimental values thus obtained fit closely to the relations of $g_0=(g_\parallel+2g_\perp)/3$, $a^V=(A^V_\parallel+2A^V_\perp)/3$, and $a^P=(A^P_\parallel+2A^P_\perp)/3$. Uncertainty in the values is as follows: $g_0(\pm 0.003)$; $g_\perp(\pm 0.004)$; $g_\parallel(\pm 0.008)$; a^V, a^P (± 1.0); $A^V_\perp, A^P_\parallel, A^P_\perp(\pm 2.0)$; $A^V_\parallel(\pm 4.0)$.

b) No significant difference was found in ESR parameters between the spectra derived from the addition of pyridine, 4-methylpyridine, and 4-cyanopyridine.

c) Shf coupling constants due to the two equivalent phosphorus nuclei (2P) and due to one phosphorus nucleus (1P).

d) Shf splitting was not observed.

$VOdtp_2$ in Pyridine Solution: The spectra observed in a pyridine solution of $VOdtp_2$ are shown in Figs. 1–C and 2–C. It can be seen that the spectra consist of eight vanadium hf lines, without any phosphorus shf splitting. Quite similar spectra were also observed in toluene solutions of $VOdtp_2$ containing a large excess of pyridine bases.

The absence of phosphorus shf splitting is taken to indicate clearly that the complex species in pyridine does not carry the coordination unit consisting of the four-membered chelate structure with the phosphorus atom located diagonally to the vanadium atom. It seems likely that pyridine causes the complete destruc-

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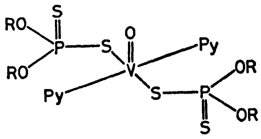
[13] The spin densities of the phosphorus 3s orbital were calculated by using a hf interaction for unit occupancy of a phosphorus 3s orbital as 3640 Gauss (P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam (1967)).

tion of the chelate structure as a result of the displacement of equatorial sulfur ligands. Thus, one can tentatively presume that the complex species in pyridine has a stoichiometry of VOdtp$_2$·Py$_2$ and such a coordination model:



[IV] VOdtp$_2$·Py$_2$

The *g*-values and vanadium hf constants (Table 1) are also interpretable on the basis of this structural model which places the unpaired electron in the vanadium 3d$_{x^2-y^2}$ orbital in the first approximation, as in the cases of VOdtp$_2$[I] and VOdtp$_2$·Py[III]. On the other hand, one might expect from the [IV] structure that the nitrogen instead of the phosphorus shf splitting is resolved. However, one may recall that oxovanadium complexes coordinated with nitrogen ligands seldom exhibit a resolved shf splitting.[5,14]

Reaction Scheme between VOdtp$_2$ and Pyridine Bases. The most important ESR information presented above is that the four-membered chelate structure of VOdtp$_2$[I] is destroyed by pyridine bases to form VOdtp$_2$·Py$_2$[III] or VOdtp$_2$·Py$_2$[IV], depending upon the concentrations of the pyridine bases in solutions. Accordingly, we can summarize the reactions of VOdtp$_2$ with pyridine bases as follows:

$$\underset{[\mathrm{I}]}{\mathrm{VOdtp_2}} + \mathrm{Py} = \underset{[\mathrm{III}]}{\mathrm{VOdtp_2 \cdot Py}} \qquad (1)$$

$$\underset{[\mathrm{III}]}{\mathrm{VOdtp_2 \cdot Py}} + \mathrm{Py} = \underset{[\mathrm{IV}]}{\mathrm{VOdtp_2 \cdot Py_2}} \qquad (2)$$

When pyridine concentrations are lower, VOdtp$_2$ reacts with the pyridine bases according to Reaction (1) to form the 1 : 1 complex, VOdtp$_2$·Py. It should be noted that Reaction (1) is not a simple process in which pyridine bases add to the open coordination position *trans* to the oxygen atom to form six-coordinate adducts. However, it seems quite possible that VOdtp$_2$·Py[III] is formed *via* an associative pathway[15] in which pyridine bases add first to the open coordination site, producing intermediate six-coordinate adducts with the [II] structure. The fact that the presence of the intermediate adduct [II] was not evidenced by ESR and optical absorption spectra probably implies that such a coordination structure is unstable and is rapidly converted into the [III] structure.

On the contrary, Reaction (2) takes place when VOdtp$_2$·Py interacts with a large excess of pyridine bases. Thus, on the dissolution of VOdtp$_2$ in pyridine, both of the four-membered chelate rings are disrupted as a result of Reactions (1) and (2) to give VOdtp$_2$·Py$_2$ with the [IV] structure. The pyridine solution of VOdtp$_2$·Py$_2$ was found to be rather unstable and to liberate slowly a blue precipitate on standing *in vacuo*.

The reaction schemes, (1) and (2), disclosed here is of particular interest because the Reaction (1) affords a marked contrast to the well-established scheme of the formation of 1 : 1 adducts of VO(acac)$_2$ with a variety of bases,[2,3] where the addition of bases occurs to the sixth position of the otherwise unaltered complex. Such a difference in the scheme of base addition arises partly from the different nature of equatorial ligands in oxovanadium complexes.

This work was supported in part by a grant of the Ministry of Education, to which the authors' grateful acknowledgements are made.

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[14] J. M. Assour, J. Goldmacher, and S. E. Harrison, *J. Chem. Phys.*, **43**, 159 (1965); M. Sato and T. Kwan, *ibid.*, **50**, 558 (1969); M. A. Hitchman, B. W. Moores, and R. L. Belford, *Inorg. Chem.*, **8**, 1817 (1969).

[15] C. H. Langford and H. B. Gray, "Ligand Substitution Process," W. A. Benjamin, New York (1965).