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Trans-Axial Ligation in Coordination Complexes of Oxovanadium(IV)[1]

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The coordination of 4-substituted pyridine 1-oxide molecules trans *to the vanadyl oxygen in several oxovanadium(IV) chelates has been investigated. Variations in the vanadium-vanadyl oxygen stretching frequencies* (ν_{v-o}) *confirm adduct formation for bis-(2,4-pentanedionato)oxovanadium(IV), bis(1-phenyl-1,3-butanedionato)oxovanadium(IV), and bis(1,1,1-trifluoro-2,4-pentanedionato)-N,N′-ethylenediaminooxovanadium(IV). For each chelate, and in a variety of solvents, a linear correlation was established between the displacement of* ν_{v-o} *upon adduct formation and a set of substituent parameters defined in terms of ligand* pK_{BH^+} *values. Bis(1,1,1-trifluoro-2,4-pentanedionato)-oxovanadium(IV) apparently forms adducts with the N-oxides, but the complex was insufficiently soluble to adequately study the variations in* ν_{v-o}. *Little, if any, adduct formation was discernable for bis(2,4-pentanedionato)-N,N′-ethylenediaminooxovanadium(IV) and bis(2,4-pentanedionato)-N,N′-1,2-propanediaminooxovanadium(IV).*

Introduction

Earlier communications[3] have dealt with the donor properties of substituted pyridine 1-oxides toward oxovanadium(IV) ions. Coordination compounds of the type VOL_5X_2, $VOL_4X_2.H_2O$, $VOL_2X_2.H_2O$, and VOL_2X_2 (L = substituted pyridine 1-oxide, X = anion) were isolated and characterized. Arguments based on infrared data for the vanadium-vanadyl oxygen stretching vibration were presented which suggested the coordination of ligands *trans* to the vanadyl oxygen in some cases, but not in others. Thus, it was of interest to study as unequivocally as possible the influence of coordination in the position *trans* to the vanadyl oxygen atom (*trans*-axial coordination).

Experimental Section

Preparation of Starting Materials. Bis(2,4-pentanedionato)-, bis(1,1,1-trifluoro-2,4-pentanedionato), and bis(1-phenyl-1,3-butanedionato)oxovanadium(IV) were prepared by the neutralization of an acidic solution of oxovanadium(IV) sulfate in the presence of the respective *beta*-diketones.[4,5] The resulting blue precipitates were collected, washed free of ionic impurities, dried, and recrystallized from benzene or toluene.

Bis(2,4-pentanedionato)oxovanadium(IV). Calculated for $VO(C_5H_7O_2)_2$: C = 45.30%, H = 5.32%. Found:[6] C = 45.34%, H = 5.28%.

Bis(1,1,1-trifluoro-2,4-pentanedionato)oxovanadium-(IV). Calculated for $VO(C_5H_4F_3O_2)_2$: C = 32.19%, H = 2.16%, F = 30.55%. Found: C = 32.26%, H = 2.30%, F = 30.27%.

Bis(1-phenyl-1,3-butanedionato)oxovanadium(IV). Calculated for $VO(C_{10}H_9O_2)_2$: C = 61.71%, H = 4.66%. Found: C = 61.73%, H = 4.61%.

The ligands, bis(2,4-pentanediono)-N,N′-1,2-propanediamine, bis(2,4-pentanediono)- and bis(1,1,1-trifluoro-2,4-pentanediono)-N,N′-ethylenediamine were prepared in a manner similar to that described by Martell, and coworkers.[7] Melting points and infrared spectra for these compounds were found to be in satisfactory agreement with those previously reported.[7,8]

Oxovanadium(IV) complexes of the quadridentate ligands were prepared from bis(2,4-pentanedionato)- and bis(1,1,1-trifluoro-2,4-pentanedionato)oxovanadium(IV), respectively, using the chelate exchange method of Martin, and collaborators.[9]

Bis(2,4-pentanedionato)-N,N′-ethylenediaminooxovanadium(IV). Calculated for $VO(C_{12}H_{18}N_2O_2)$: C = 49.83%, H = 6.27%, N = 9.69%. Found: C = 49.85%, H = 6.25%, N = 9.55%.

Bis(2,4-pentanedionato)-N,N′-1,2-propanediaminooxovanadium(IV). Calculated for $VO(C_{13}H_{20}N_2O_2)$: C = 51.49%, H = 6.65%, N = 9.24%. Found: C = 51.42%, H = 6.58%, N = 9.05%.

Bis(1,1,1-trifluoro-2,4-pentanedionato)N,N′-ethylenediaminooxovanadium(IV). Calculated for $VO(C_{12}H_{12}$-

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[2] National Aeronautics and Space Administration Predoctoral Trainee (1963-1966).

[3] (a) R. G. Garvey and R. O. Ragsdale, *Inorg. Chem.*, *4*, 1604 (1965); (b) R. G. Garvey and R. O. Ragsdale, *J. Inorg. Nucl. Chem.*, *29*, 745 (1967).

[4] R. A. Rowe and M. M. Jones, *Inorg. Syn.*, *5*, 115 (1957).

[5] D. F. Martin and K. Ramaiah, *J. Inorg. Nucl. Chem.*, *27*, 2027 (1965).

[6] All microanalyses were performed by Alfred Bernhardt Microanalytical Laboratories, Mulheim (Ruhr) Germany.

[7] A. E. Martell, P. J. McCarthy, R. J. Hovey, and K. Ueno, *J. Am. Chem. Soc.*, *77*, 5820 (1955).

[8] K. Ueno and A. E. Martell, *J. Phys. Chem.*, *59*, 998 (1955).

[9] K. Ramaiah, F. E. Anderson, and D. F. Martin, *Inorg. Chem.*, *3*, 296 (1964); A. W. Struss and D. F. Martin, *J. Inorg. Nucl. Chem.*, *25*, 1409 (1963); K. Ramaiah and D. F. Martin, *Ibid.*, *27*, 1663 (1965).

$F_6N_2O_2$): C=36.22%, H=3.24%, N=7.04%, F=28.65%. Found: C=36.05%, H=3.20%, N=7.18%, F=28.47%.

4-Methoxy-, 4-methyl-, 4-nitro, and the parent pyridine 1-oxides were obtained commercially The 4-methoxy substituted compound was recrystallized from an acetone-ether solvent prior to use. Pyridine 1-oxide was resublimed under reduced pressure. The remaining N-oxides were employed directly. 4-Bromo- and 4-chloropyridine 1-oxides were prepared by treating the 4-nitro substituted compound with the appropriate acetyl halide.[10] 4-Carbomethoxy pyridine 1-oxide was prepared via peroxide oxidation of the corresponding pyridine[11] and 4-N,N-dimethylaminopyridine 1-oxide from the reaction of 4-chloropyridine 1-oxide with dimethylamine.[11]

Procedure for Spectrophotometric Studies. Stock solutions of the appropriate oxovanadium(IV) compounds were prepared in diverse solvents. For each system investigated, successive portions of a base donor were added to one aliquot of the respective oxovanadium(IV) stock solution. The infrared and/or the visible spectra were then recorded for each solution after each addition. The formation of an adduct could thus be followed by the development of bands not previously observed in either the spectrum for the free chelate or that for the free ligand.

No decomposition of the oxovanadium(IV) adducts was noted over periods well beyond those necessary for recording of their spectra. Subsequently, however, decomposition was indicated by the formation of dark residues and by changes in both the infrared and visible spectra of the solutions.[12]

Infrared spectra were recorded on a Beckman IR-4 recording spectrophotometer equipped with sodium chloride optics or on a Perkin-Elmer model 421 grating spectrophotometer. Visible spectra were obtained on a Cary model 14 recording spectrophotometer.

Results and Discussion

Displacements of the vanadium-vanadyl oxygen stretching band, ν_{v-o}, upon coordination of substituted pyridine 1-oxides with bis(2,4-pentanedionato)oxovanadium(IV) in dichloromethane are illustrated in Figure 1. Addition of successive portions of the base brought about a reduction in the intensity of band A, the unperturbed value of ν_{v-o}, and a concomitant increase in the intensity of the adduct bands indicated by B. Analogous spectral changes were observed in acetonitrile, bromoform, and chloroform.

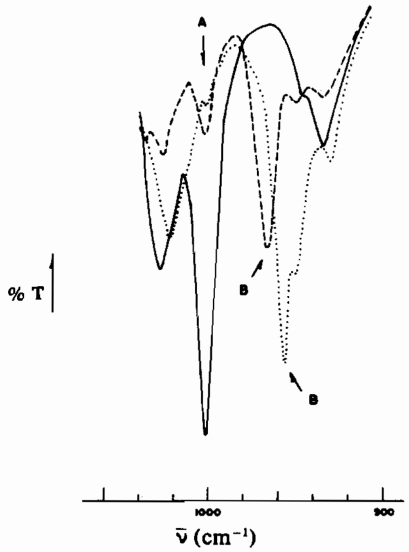

Figure 1. Infrared spectra of bis(2,4-pentanedionato)oxovanadium(IV) in dichloromethane (——) showing the effect of adding approximately 1 to 1 mole ratios of 4-methyl- (· · ·) and 4-chloro (- - -) pyridine 1-oxides. ν_{v-o} for the unperturbed (A) and adduct (B) bands are indicated.

The square pyramidal structure of bis(2,4-pentanedionato)oxovanadium(IV),[14,15] bis(1-phenyl-1,3-butanedionato-),[15,16] and presumably bis(1,3-diphenyl-1,3-propanedionato)-[17] and bis(1,1,1-trifluoro-2,4-pentanedionato)oxovanadium(IV),[18] is clearly susceptible to the coordination of diverse donor molecules *trans* to the vanadyl oxygen atom.[18-21] This property has evoked numerous attempts to utilize bis(2,4-pentanedionato)oxovanadium(IV) as a reference acid in establishing a quantitative measure of base donor strengths [18,19,21] Carlin and Walker,[18] for example, found a linear relationship between the stability constants of its adducts with several substituted pyridines and the respective pK_{BH^+} values of the pyridines.

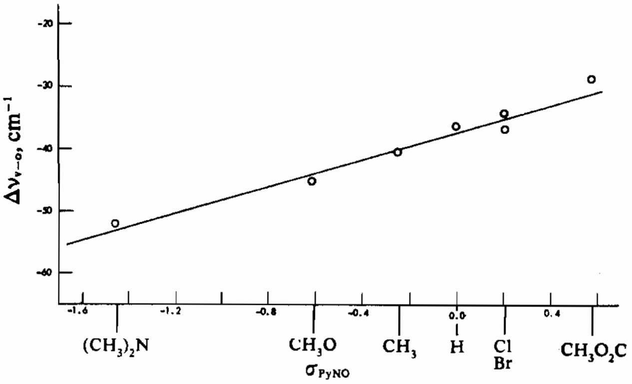

Figure 2. Variation of $\Delta\nu_{v-o}$ with σ_{PyNO} values of 4-substituted pyridine l-oxide adducts with bis(2,4-pentanedionato)oxovanadium(IV).

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(10) E. Ochiai, *J. Org. Chem.*, *18*, 534 (1953).

(11) A. R. Katritzky, *J. Chem. Soc.*, 2404 (1956).

(12) Selbin, *et al.*[13] have reported a spectrophotometric study of the spectral changes associated with the oxidation of bis(2,4-pentanedionato)oxovanadium(IV) in polar solvent systems.

(13) T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, *41*, 262 (1964).

(14) R. P. Dodge, D. H. Templeton, and A. Zalkin, *J. Chem. Phys.*, *35*, 55 (1961).

(15) P. K. Hon, R. L. Belford, and C. E. Pfluger, *ibid.*, *43*, 3111 (1965).

(16) *Ibid.*, *43*, 1323 (1965).

(17) S. Ikeda, A. Yamamoto, S. Kurita, K. Takahashi, and T. Watanabe, *Inorg. Chem.*, *5*, 646 (1966).

(18) R. L. Carlin and F. A. Walker, *J. Am. Chem. Soc.*, *87*, 2128 (1965).

(19) M. M. Jones, *Naturforschung*, *12b*, 595 (1957); M. M. Jones, *J. Am. Chem. Soc.*, *76*, 5995 (1954); R. T. Claunch, T. W. Martin, and M. M. Jones, *ibid.*, *83*, 1673 (1961).

(20) K. Nakamoto, Y. Morimoto, and A. E. Martell, *ibid.*, *83*, 4533 (1961).

(21) J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, *26*, 37 (1964).

In Figure 2 a linear correlation of $\Delta\nu_{v-o}$ (defined as ν_{v-o} for the N-oxide adduct minus ν_{v-o} for the free acid) with a set of substituent parameters, σ_{PyNO},[22] has been established. This set of constants was derived from the acid dissociation constants of the protonated substituted pyridine 1-oxides.[23] Higher negative values of $\Delta\nu_{v-o}$ indicates a concurrent decrease in the vanadium-vanadyl oxygen "bond order" as the 4-substituent becomes more activating.

No points for the highly deactivator substituted pyridine 1-oxide, 4-nitropyridine 1-oxide, are included in the correlation of Figure 2. Under the experimental conditions employed, no absorption band assignable to ν_{v-o} of the adduct was discernable. Moreover, adduct formation with saturated solutions of 4-carbomethoxypyridine 1-oxide is discernable by the infrared technique. Thus, the more negative pK_{BH^+} of 4-nitropyridine 1-oxide (−1.7)[24] *versus* −0.41 for the carbomethoxy compound[25] and its lesser solubility are in accord with the fact, no evidence of adduct formation was recorded.

Similar plots of $\Delta\nu_{v-o}$ values are shown in Figure 3 for the complexes bis(1,1,1-trifluoro-2,4-pentanedionato)oxovanadium(IV) and bis(1-phenyl-1,3-butanedionato)oxovanadium(IV). The anomalous behavior of the trifluoromethyl substituted compound in formation of adducts with the pyridine 1-oxides would seem to be related to the electronic distortions introduced by the fluorine atoms. Rather pronounced changes in the carbonyl and carbon-carbon double bond stretching frequencies are noted for copper(II) and nickel(II)complexes with *beta*-diketones when a methyl group is replaced with a trifluoromethyl group.[26] On the other hand, substitution of a phenyl group has only a slight effect on these same bands. The change in ν_{v-o} upon replacing a methyl group with a trifluoromethyl group in bis(*beta*-diketonato)oxovanadium(IV) acids is very pronounced (ν_{v-o} shifts from about 999 cm.$^{-1}$ to 930 cm.$^{-1}$ for spectra recorded from potassium bromide disks[9] and Nujol mulls or to 972 cm.$^{-1}$ in acetonitrile). Substitution of a phenyl group has, as before, little effect (ν_{v-o} occurs at 995 cm.$^{-1}$ for spectra recorded from potassium bromide disks and Nujol mulls or at 999 cm^{-1} in dichloromethane).

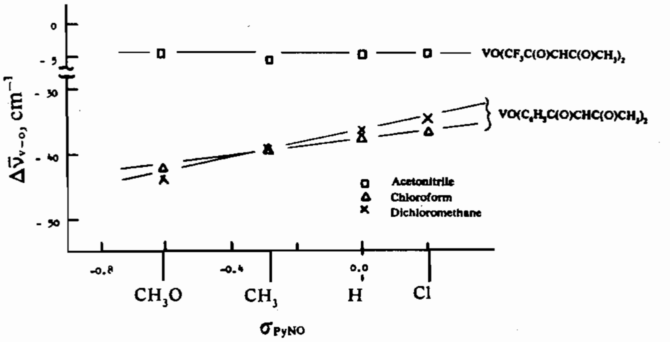

Figure 3. Variation of $\Delta\nu_{v-o}$ with σ_{PyNO} values of 4-substituted pyridine 1-oxides interacting with bis(1,1,1-trifluoro-2,4-pentanedionato)oxovanadium(IV), {VO(CF$_3$C(O)CHC(O)CH$_3$)$_2$} and bis(1-phenyl-1,3-butanedionato)oxovanadium(IV), {VO-(C$_6$H$_5$C(O)CHC(O)CH$_3$)$_2$}.

4-Substituted pyridine 1-oxides appear to be ineffective in displacing a solvent molecule from the *trans*-axial site of bis(1,1,1-trifluoro-2,4-pentanedionato)-oxovanadium(IV) in acetonitrile. In less basic solvents, adduct formation does occur as suggested in Figure 4. The shifts in optical absorption maxima for the latter complex upon adduct formation are similar to those for bis(2,4-pentanedionato)oxovanadium(IV). However, the trifluoromethyl substituted compound has limited solubility in the halocarbon solvents. Thus the effect of adduct formation on ν_{v-o} could not be assessed.

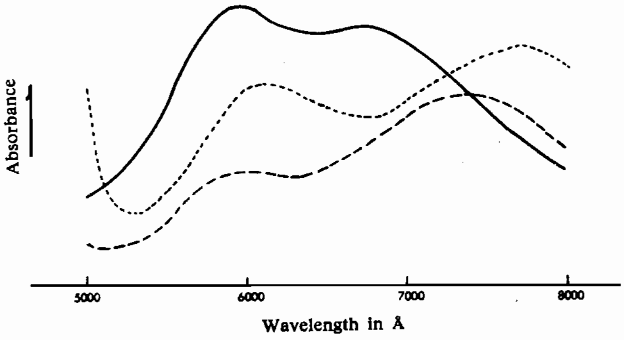

Figure 4. Solution spectra of bis(1,1,1-trifluoro-2,4-pentanedionato)oxovanadium(IV) in dichloromethane (——) and its adducts with acetonitrile (---) and 4-methylpyridine 1-oxide (· · ·).

Values of $\Delta\nu_{v-o}$ for bis(2,4-pentanedionato)-N,N′-ethylene- and bis(2,4-pentanedionato)-N,N′-1,2-propanediaminooxovanadium(IV) in the presence of the substituted pyridine 1-oxides suggest little, if any, adduct formation occurs (Figure 5). Furthermore, no essential changes were observed for the corresponding visible spectra of these two systems. Apparently the *trans* axial position is much less available for coordination in these compounds. Based upon similar observations, it was suggested that in solution bis(salicylaldato)-N,N′-ethylenediaminooxovanadium(IV) may exist in a pyramidal structure distorted such that no sixth coordination position remained accessible for adduct formation.[27]

Interestingly though, upon including both *cis*-trifluoromethyl groups[28] and *cis*-nitrogen donors in the equatorial chelate moiety of bis(1,1,1-trifluoro-2,4-pentanedionato)-N,N′-ethylenediaminooxovanadium(IV), ν_{v-o} returns to the range observed for bis(2,4-pentanedionato)oxovanadium(IV) (*i.e.*, 996 cm.$^{-1}$ for a

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[22] J. H. Nelson, R. G. Garvey, and R. O. Ragsdale, *J. Heterocyclic Chem.*, 4, 591 (1967).

[23] S. I. Shupack and M. Orchin, *J. Am. Chem. Soc.*, 85, 902 (1963) found similar σ_P parameters accurately portray the trends in pK_a values for the 4-substituted pyridine 1-oxides. However, these authors used a hybrid set of parameters drawn from σ^+, σ, and σ^- values.

[24] H. H. Jaffe and G. O. Doak, *J. Am. Chem. Soc.*, 77, 4441 (1955).

[25] T. Kubota and H. Miyazaki, *Bull. Chem. Soc. Japan*, 39, 2057 (1966).

[26] K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Phys. Chem.*, 66, 346 (1962).

[27] J. Selbin, H. R. Manning, and G. Cessac, *J. Inorg. Nucl. Chem.*, 25, 1253 (1963).

[28] R. J. Hovey and A. E. Martell, *J. Am. Chem. Soc.*, 82, 2697 (1960).

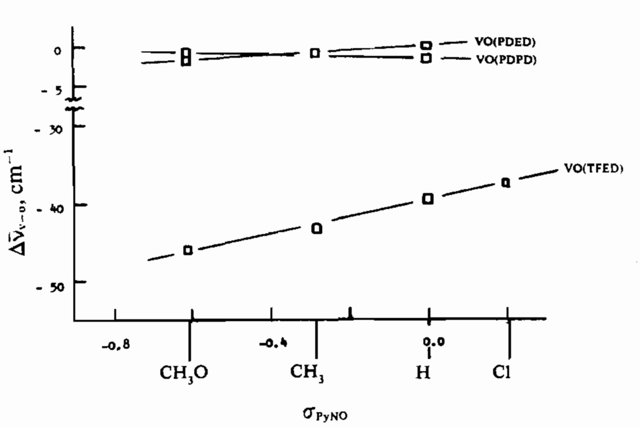

Figure 5. Variation of $\Delta\nu_{v-o}$ with σ_{PyNO} values of 4-substituted pyridine 1-oxides in acetonitrile interacting with bis(2,4-pentanedionato)-N,N'-ethylenediaminooxovanadium(IV), {VO(PDED)}; bis(2,4-pentanedionato)-N,N'-1,2-propanediaminooxovanadium(IV), {VO(PDPD)}; and bis(1,1,1-trifluoro-2,4-pentanedionato)-N,N'-ethylenediaminooxovanadium(IV), {VO-(TFED)}.

Nujol mull or 1003 cm.$^{-1}$ for an acetonitrile solution). This implies the possibility that the electronic and structural distortions present in the "component chelates" are responsible for the anomalous values of ν_{v-o} and for the seeming lack of N-oxide coordination. A mutual cancellation of these effects could occur allowing the normal substituent perturbation of $\Delta\nu_{v-o}$ to be manifest, as before.

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