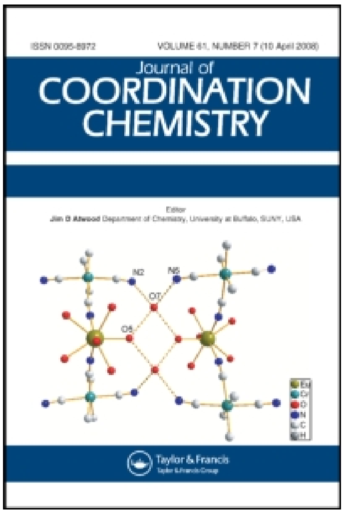
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SPECTROSCOPIC, ELECTROCHEMICAL AND QUANTUM MECHANICAL INVESTIGATIONS OF VANADYL(IV)-ACETYLACETONATE IN NON-AQUEOUS SOLUTIONS

Wolfgang Linert[a]; Erwin Herlinger[a]; Peter Margl[a]; Roman Bočka[b]
[a] Institute of Inorganic Chemistry, Technical University of Vienna, Vienna, Austria [b] Department of Inorganic Chemistry, Slovak Technical University, Bratislava, Czechoslovakia

To cite this Article Linert, Wolfgang , Herlinger, Erwin , Margl, Peter and Bočka, Roman(1993) 'SPECTROSCOPIC, ELECTROCHEMICAL AND QUANTUM MECHANICAL INVESTIGATIONS OF VANADYL(IV)-ACETYLACETONATE IN NON-AQUEOUS SOLUTIONS', Journal of Coordination Chemistry, 28: 1, 1 — 16

To link to this Article: DOI: 10.1080/00958979308035139

URL: http://dx.doi.org/10.1080/00958979308035139

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1993, Vol. 28, pp. 1–16
Reprints available directly from the publisher
Photocopying permitted by licence only

© 1993 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

SPECTROSCOPIC, ELECTROCHEMICAL AND QUANTUM MECHANICAL INVESTIGATIONS OF VANADYL(IV)-ACETYLACETONATE IN NON-AQUEOUS SOLUTIONS

WOLFGANG LINERT,* ERWIN HERLINGER and PETER MARGL

Institute of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria

and ROMAN BOČA

Department of Inorganic Chemistry, Slovak Technical University, CS-81237, Bratislava, Czechoslovakia

(*Received February 21, 1992*)

Adduct formation between bis(acetylacetonato)oxovanadium(IV), ($VO(acac)_2$), and various solvents has been studied. Electronic, IR- and Far IR spectra are reported and interpreted in terms of solvate formation. Formation constants are estimated from Far IR-spectra. Evidence was obtained for a *cis-trans*-equilibrium of pyridine solvates in solution. The 1:1-adducts with pyridine, *N,N*-dimethylformamide, *N,N*-dimethylacetamide and dimethylsulfoxide were obtained in crystalline form. Acetonitrile, acetone and diethylketone formed non-stoichiometric solvates. Cyclic voltammetric data in different solvents are reported and interpreted.

Keywords: solvatochromism, vibrational spectroscopy, quasirelativistic INDO-calculations, vanadium(IV), acetylacetone

Downloaded At: 17:38 23 January 2011

INTRODUCTION

Vanadyl(IV)-acetylacetonate [$VO(acac)_2$] is known to interact with various donor solvents, exhibiting solvatochromic behaviour.[1] The solvation reaction leads to a colour change from blue to green.[2,3] By analogy to compounds like mixed Cu(II) and Ni(II) tetramethylethylenediamine-acetylacetonate complexes[4,5] or trimethylchlorostannane,[6,7] we expected structural variations with dependence on solvent. In order to investigate these effects, spectroscopic and electrochemical methods have been applied in combination with semi-empirical quantum-mechanical calculations using the INDO approach.

METHODS

Vanadyl acetylacetonate [$VO(acac)_2$] was prepared according to the literature[8] and recrystallised from dichloromethane,[9] yielding large blue-green crystals. Solid

---

* Author for correspondence.

1:1-solvates $VO(acac)_2 \cdot Solv$ with *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) were prepared by dropwise addition of these solvents in slight molar excess to about 10 g of $VO(acac)_2$. The mixture turned green and was heated with constant stirring until it became clear. Some minutes after the dissolution process was completed, solid $VO(acac)_2 \cdot Solv$ precipitated quickly as fine, green crystals. The pyridine (Py) solvate[10,11] was obtained by the same procedure but needed precipitation of the solvate with dry ether. The precipitate was kept at 5°C for 24 h before filtration. The solvate with dimethylsulfoxide (DMSO) was precipitated by slow evaporation of the solvent under reduced pressure. The solids were dried under reduced pressure at room temperature for several days. The purity of products has been tested by microanalysis (Table I). Syntheses were carried out under dry nitrogen atmosphere to avoid formation of V_2O_5. All adducts except the pyridine adduct are very susceptible to heat, showing a quick colour change from green to blue due to dissociation into $VO(acac)_2$ and free solvent, and show no defined melting points.

IR spectra were recorded on Bruker IFS 88 (solid state) and Perkin Elmer 16PC (solutions) spectrophotometers. Far-IR spectra were measured with a Nicolet 20F Fourier transform spectrometer. The solvents used were purified according to standard methods. Water content was determined by Karl Fischer titration. For solution IR and Far IR measurements, cells with NaCl and polyethylene windows, respectively, were used. Solid state IR spectroscopy of the adducts was carried out with KBr pellets; the solid adduct compounds were ground at the temperature of liquid nitrogen, the pressing tools were kept at -20°C. Nujol mull treatment led to decomposition of the adducts. Solid state Far IR spectra were measured in polyethylene pellets. During Far IR solid state measurements, the cell was cooled with N_2 directly evaporated from liquid nitrogen. The optical bench was held under reduced pressure (< 0.3 Torr) to avoid the IR absorption of water vapour within the spectrometer. For IR and Far IR measurements in solution, concentrations of about 5 mM were used.

Electronic spectra were recorded with a Hitachi U-2000 spectrophotometer equipped with a thermoelectric cell holder. The temperature was kept at 25°C and similar precautions as in the IR and Far IR measurements were taken.

Electrochemical investigations were carried out using a non-isothermal cell arrangement with a silver-wire reference electrode kept at constant temperature.[12,13] Cyclic voltammetry was performed on platinum as well as on carbon-glass electrodes, yielding essentially the same results. Polarographic redox potentials were recorded with respect to bis(biphenyl)chromium(I) tetraphenyloborate (BBCr)[14] either

TABLE I
Results of elementary analysis (%) of the 1:1 solvates $VO(acac)_2 \cdot Solv$ (calculated values given in parentheses).

Solv	C	H	N
	45.5 (45.3)	5.0 (5.3)	
DMF	46.2 (46.2)	5.8 (6.3)	3.8 (4.2)
DMA	48.0 (47.7)	6.2 (6.6)	4.0 (4.0)
DMSO	42.0 (41.8)	5.9 (5.5)	
Pyridine	52.6 (52.3)	5.3 (5.6)	4.1 (4.0)

Downloaded At: 17:38 23 January 2011

directly or *via* ferrocene as intermediate reference substance. Solutions containing 0.1 mM of the respective complex and 0.1 M $[NBu_4][BPh_4]$ were placed in a thermostatted double-sided cell and pure nitrogen, pre-saturated with solvent, passed through the solution during the experiment.

Quantum chemical calculations were performed on a IBM-ES/9021-720 computer using a *quasi*-relativistic INDO program.[15] This program includes a non-empirical version of the CNDO/1 method and includes dominant relativistic effects[16,17] as well as one electron corrections.[18] Therefore it is able to make calculations on systems containing heavy transition metal ions[19] and to consider solvation effects.[20] Geometry was based on X-ray diffraction data and optimized to obtain minimal total energies (see below).

RESULTS AND DISCUSSION

By the method described above, three adducts of $VO(acac)_2$ could be prepared, namely with DMSO, DMF and DMA. Their thermal stability ascends in the order DMSO $<$ DMF $\ll$ DMA ($<$ Pyridine). The adduct with DMSO is, despite the rather high donor number of DMSO (29.8) the most unstable in this series.

Attempts were made to prepare diethylketone (DN $\sim$ 18), acetone and acetonitrile (DN = 17.1 and 14) adducts in the same manner, but the solid precipitate obtained still contained about 50% $VO(acac)_2$, thus yielding broad and flat bands in the IR spectra. That these adducts were not wet was assured by drying for several days in high vacuum. After this treatment the compounds still decomposed below 60°C (mp of pure $VO(acac)_2$: 245°C). Therefore no spectroscopic results can be given for these compounds.

Downloaded At: 17:38 23 January 2011

In dioxane and THF solutions, $VO(acac)_2$ reacts with dissolved oxygen as indicated by a rapid colour change from green to red.[21,22] The red colour disappears when nitrogen is passed through the solution, but a yellow colour appears instead. This latter process is reversible. The Far IR spectra in these two solvents show a greater shift than expected from the DN. This suggests the coordination of molecular oxygen to the vanadium atom, followed by oxidation and reversible adduct formation at the vanadium(V) moiety. The electronic spectrum resembles spectra in which a peroxide group is coordinated to vanadium(V).[23] Such O_2 adducts have been reported by Sawyer *et al.*[24] for methanolic solutions of $VO(acac)_2$ in the presence of di-*tert*-butylcatechol. Their results, however, have been questioned by others.[25] Further investigations to elucidate this reaction are in progress in our laboratories.

Electronic Spectra

The spectra are in agreement with earlier results.[2,3,9,26] The two-electron transfer absorption bands, assigned to $^2B_2 \rightarrow 2E(I)$ $(d_{xy} \rightarrow d_{xz,yz})$ and $^2B_2 \rightarrow {}^1B_1$ $(d_{xy \rightarrow x^2-y^2})$ transitions,[27,28] are found in the visible region and their positions are given for various solvents in Table II. The $^2B_2 \rightarrow {}^2A_1$ $(d_{xy \rightarrow z^2})$ transitions are not given because they are in most cases only visible as shoulders of an intense charge-transfer band.[27]

Figure 1 shows the dependence of wavelength of the $^2B_2 \rightarrow {}^2E(I)$ transition on donor number. In solvents of donor numbers smaller than 10 the spectra refer to the five-coordinate $VO(acac)_2$ species without coordination of solvent. Above a

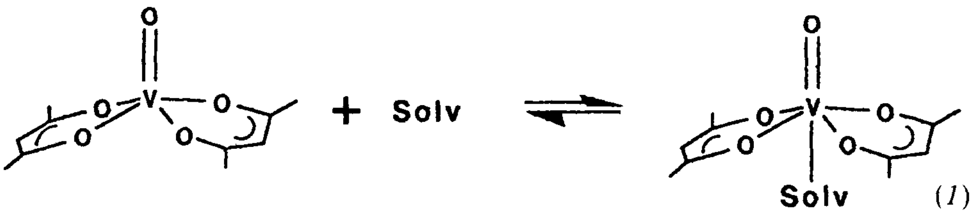
TABLE II
Position of the absorption maxima of the electronic spectra of VO(acac)$_2$ in various donor solvents.

	DN	λ ($^2B_2 \rightarrow 2E(I)$)/nm	λ ($^2B_2 \rightarrow {}^1B_1$)/nm
CH_2Cl_2	0[a]	668.5	594.0
$CHCl_3$	0[a]	671.0	595.5
DCE	0.0	678.0	602.0
Benzene	0.1	663.0	596.0
Nitromethane	2.7	684.5	602.0
Nitroethane	2.7[a]	679.0	596.0
Nitrobenzene	4.4	678.0	599.0
Benzonitrile	11.9	683.0	596.0
Acetonitrile	14.1	699.5	593.5
Dioxane	14.8	724.0	583.0
PDC	15.1	704.0	595.0
Benzylcyanide	15.1	694.5	594.0
Ethylenesulfite	15.3	729.0	596.0
Propionitrile	16.1	686.0	602.5
Water	16.4	813.0	563.5
MeOAc	16.5	678.0	595.5
Acetone	17.0	693.0	595.0
Hacac		701.0	571.5
n-$BuNH_2$		758.0	578.5
Piperidine		759.0	585.0
n-BuOH	~18[a]	761.5	582.0
MeOH	19	773.5	602.0
EtOH	~20[a]	774.5	579.5
NMF	~25[a]	788.5	585.5
TMP	23.0	767.0	584.0
DMF	26.6	769.0	590.0
NMP	27.3	767.0	593.0
DMA	27.8	771.5	594.5
TMU	29.6	766.0	596.0
DMSO	29.8	779.0	588.0
DEF	30.9	760.0	590.0
DEA	32.1	767.0	594.0
Pyridine	33.1	764.0	578.0

[a] Estimated value.

Downloaded At: 17:38 23 January 2011

donor number of 20 the vanadium(V) coordination centre has a distorted octahedral coordination including one coordinated solvent according to (*1*).



(I) (II) (*1*)

Between a donor number of 10 to 20 both (**I**) and (**II**) are present in considerable amounts. However, the expected two absorption maxima could not be separated.

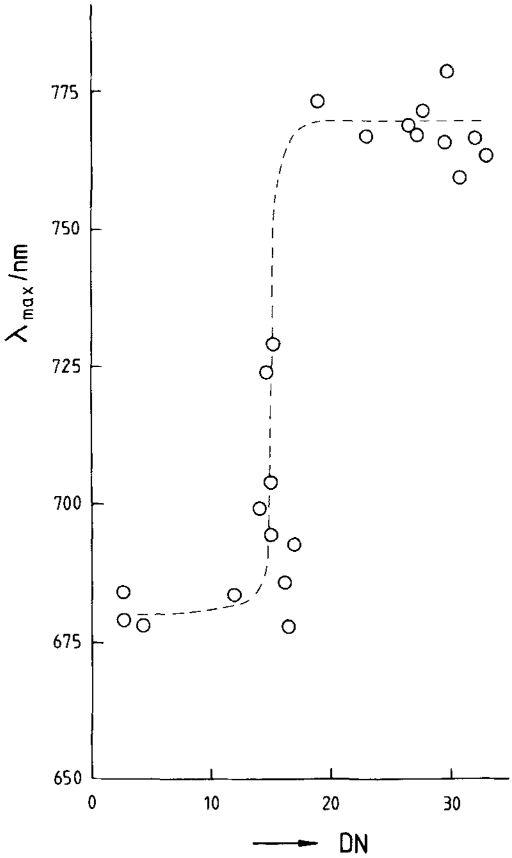


FIGURE 1 Absorption maxima of the $^2B_2 \rightarrow {}^2E(1)$ transition *versus* donor number of the solvent.

Downloaded At: 17:38 23 January 2011

The values for the absorption maxima therefore refer to the observed absorption band representing the overlap of the two species. The shift of the band is due to changing intensities of the two overlapping bands associated with the changing concentration of the two species. Larger shifts are seen for hydroxylic solvents like water or methanol as can be expected from their more pronounced acceptor properties. This fact is supported by ESR measurements with ethanol where signs of simultaneous coordination *via* a hydrogen bond are found.[21] The solvatochromism of the system can be compared with that of Ni(acac)(tmen)$^{2+}$,[4,5] where the colour change seen in the visible region is due to a change in the inner coordination sphere. This explains the step-like character depicted in Figure 1. Changes of spectra of coordinated and uncoordinated species due to changes in the ligand field are hardly pronounced. This may be explained by results from the INDO-calculations, namely that the optical excitation takes place at an unpaired electron positioned in the d_{xy} orbital of the vanadium centre and the fact that this orbital is not involved directly in the binding of a solvent molecule.

TABLE III
IR data for $VO(acac)_2$ in various donor solvents and for the solid adducts.

	Solution		Solid state
	$\nu^{free}_{V=O}/cm^{-1}$	$\nu^{coord}_{V=O}/cm^{-1}$	$\nu^{coord}_{V=O}/cm^{-1}$
DCE		1002	
CCl_4		1008	
Benzene		1006	
Nitromethane		1000	
Nitrobenzene		1002	
Benzonitrile		1003	
Acetonitrile	995	986	
Dioxan		990	985[a]
Acetone	990	1000	
MeOH	992	1006	
THF	990	1007	*
DMF		971	966
NMP		972	
DMA		971	964
DMSO		971	*
DEF		973	*
Pyridine	988	970	965

[a] Ref. 29.
* Decomposition of the substance.

Downloaded At: 17:38 23 January 2011

IR Spectra

The V=O stretching vibration shifts from 1002 cm^{-1} for non-coordinating solvents to 970 cm^{-1} in strongly coordinating solvents.[3,10] In the present paper, V=O stretching vibrations are reported for 17 solvents (Table III). A splitting of the $\nu_{V=O}$ band in solvents of intermediate donor strength (An, MeOH, PN, THF and acetone) indicates the existence of equilibrium (*1*) and can be interpreted, as above, as being due to the presence of both uncoordinated and coordinated species in comparable amounts. A linear relationship is found between the IR absorption frequency of the coordinated species and Gutmann's Donor Number (DN).[30] This indicates a weakening of the V=O bond by electron-pair donation from a coordinating solvent molecule.

Far IR Spectra

The assignments of FIR absorption bands (Table IV) was based on a study by Vlckova *et al.*,[31] except that we attribute the band at 366 cm^{-1} to the B_2 $\nu(VO_4)$ mode. This is justified by results found with this assumption for bond angles using the method of Beck *et al.*[32] The approach requires a intensity ratio between B_2/A_1 of about 6.0 for non-coordinated $VO(acac)_2$ and much higher ratios for medium and strongly coordinated species. This cannot possibly be achieved with the preceding normal coordinate analyses. It is remarkable that one band shows a strong solvatochromic shift in the FIR region (B_1 at 484–462 cm^{-1}), which is obviously split in solvents of intermediate donor strength, where an equilibrium between coordinated and uncoordinated species exists. With increasing donor number this

Downloaded At: 17:38 23 January 2011

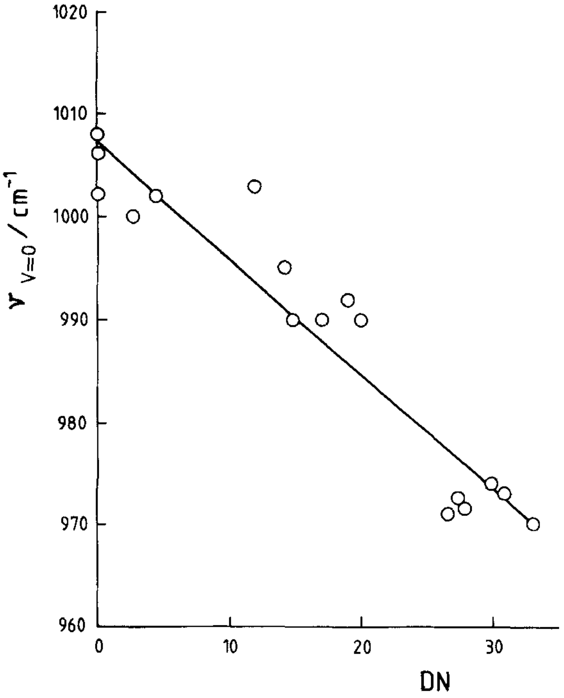


FIGURE 2 The ν(V=O) absorption frequency of solvated VO(acac)$_2$·Solv *versus* the donor number.

band is shifted from 485 cm^{-1} (DCE) to 460 cm^{-1} (Pyridine). All other bands shift considerably less. However, all Far IR shifts demonstrate that all V–O bonds are considerably weakened on coordination of a donor solvent in the sixth ligand position (in agreement with Gutmann's bond length variation rule[30]).

The characteristic section of the Far IR spectra is given in Figure 3. The figure shows that the combined V–O stretching vibrations of the vanadium coordination centre with the acetylacetonate oxygen atoms (abbreviated as ν_{VO_4}) is shifted when coordination of a solvent takes place.

As for the IR spectra the equilibrium between the VO(acac)$_2$ and VO(acac)$_2$·Solv is seen in the form of separable bands. From the integral ratio of the most intense absorption bands arising from the $\nu_{VO_4}(A_1)$ stretching vibration of the free VO(acac)$_2$ and of the coordinated VO(acac)$_2$·Solv species, formation constants can be calculated with the sound assumption that the absorption coefficient of this vibration is the same for both species (see Table III). The values obtained largely confirm the values obtained by Gutmann and Mayer[9] and they can be taken in continuation of their values towards lower donor numbers. They used solutions where the donor solvent was diluted in CH_2Cl_2, whose DN should be close to zero, and in An whose donor number of 14.1 shows significant ability to coordinate in concurrence to other solvents to VO(acac)$_2$.

For both weak donor solvents (DN < 13) almost no frequency shift is observed. Intermediate donors (14 < DN < 21) show bands for uncoordinated VO(acac)$_2$ and coordinated VO(acac)$_2$·Solv. In strong donor solvents (DN > 21) only the band of the coordinated species is found. Complex formation constants are given in Table V.

Downloaded At: 17:38 23 January 2011

TABLE IV

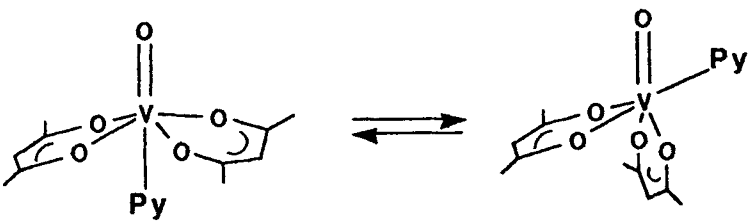
Far IR absorption maxima (in cm^{-1}) of VO(acac)$_2$ in solution and of solid state 1:1 solvates with various solvents (vw: very weak; w: weak; m: medium; s: strong).

Solvent	$\nu_{V=O}$	ν_{VO_4} (A$_2$)	ν_{VO_4} (B$_1$)	ν_{VO_4} (A$_1$)	δ_{O-V-O}	ν_{VO_4} (B$_2$)
			Spectra measured in solution			
1,2-Dichloroethane	606.1 w	560.0 vw	484.5 s	462.4 w	425.9 w	367.3 m
Benzene	612.7 m	528.4 m	484.0 vs	462.9 w	424.9 w	366.3 m
Nitromethane	a	a	a	463.2 m	427.1 s	368.4 s
Nitrobenzene	608.1 w	530.1 s	484.3 m	462.4 vw	426.0 w	391.77 w; 367.1 w
Bromobenzene	607.0 w	a	484.0 vs	461.8 s	425.0 w	366.61
Acetonitrile	610.0 vw; 606.3 w	552.5 vw; 561.0 vw	485.7 s; 474.2 s	455.0 w	425.8 w	366.0 w
Propionitrile	605.9 m[b]	545.0 w	485.2 s; 472.7 m	455.0 w	425.4 w	380.9 w; 366.6 m
Dioxane			471.27	455.04		364.4
Acetone	616.2 m; 603.6 m	a	484.4 s; 471.5 s	453.1 m	426.4 m	366.3 m
Ethylacetate	a	a	484.1 s; 470.5 m	453.0 w	424.0 w	a
Methanol	a	a	460.2 s	453.0 m	421.3 m	365.3 m
Tetrahydrofurane	618.6 w; 602.4 m		482.8 m; 468.7 s	453.0 w	420.6 w	363.6 m
N,N-Dimethylformamide	600.5 w		463.1 s	450.0 w[a]	420.6 w; 403.3 vw	380.7 w; 370.1 s
N,N-Dimethylacetamide	617.7 w	547.9 vw	483.5 w; 460.6 vs	449.8 w	420.5 w	362.4 m
N,N-Diethylformamide	598.7 w	546.1 cw	461.3 vs	449.8 w	420.5 m	362.5 m
Dimethylsulfoxide	599.8 w	548.6 vw	483.0 vw; 460.9 s	449.8 w	420.5 w	362.5 m
Pyridine	638.2 w; 618.8 w	555.7 w; 547.8 w	464.3 m; 454.4 s	441.5 m; 431.2 m	413.0 vw	358.8 vw; 348.4 s; 355.0 vw
			Spectra from solid state solvates			
Free VO(acac)$_2$	607.9 m	561.2 vw	483.1 s	463.1 m	424.3 m	366.4 m
N,N-Dimethylformamide	627.0 w; 596.2 s	564.2 vw	482.6 w; 459.4 s	467.2 vw	418.8 m	380.0 m; 358.7 m
N,N-Dimethylacetamide	627.7 w; 595.3 s[b]	569.4 m; 542.9 m	482.2 m; 453.0 s	540.0 w	419.2 m	359.7 s
Dimethylsulfoxide	630.3 w; 597.6 s	472.0 m; 535.99 w	479.7 m; 462.9 s	450.9 w	409.0m	362.5 s
Pyridine	612.1 m; 598.4 m	464.0 w, 541.0 vw	488.8 w; 467.2 s	450.2 m	418.4 w; 418.7 m	361.4 m; 348.4 w

[a] Not accessible because of solvent absorption.

[b] Broad.

The Far IR-spectra of VO(acac)$_2$ in pyridine solution shows a splitting of these bands, a fact which can be attributed to a *cis-trans*-equilibrium in solution, as has been found in solid adducts of VO(acac)$_2$ with a series of substituted pyridines.[10] From the intensities of both peaks we conclude that a ratio of about 2:1 for the concentrations of species (**III**) and (**IV**) is present in pyridine solution.



(**III**) (**IV**)

From Far IR spectra, bond angles at the coordination centre can be obtained.[6,7] From the C_{2v} symmetry of the VO(acac)$_2$ molecule, one can derive the relationships (*2*)[32] and (*3*).

$$\frac{I_{B_2}}{I_{A_1}} = \left(\frac{\cos\frac{\beta}{2}\sin\frac{\gamma}{2}}{\cos\frac{\beta}{2}\cos\frac{\gamma}{2}} \right)^2 \qquad (2)$$

$$\alpha = 90 + \arcsin\left[\sin\left(90 - \frac{\beta}{2}\right) \sin\left(90 - \frac{\gamma}{2}\right) \right] \qquad (3)$$

TABLE V

Complex formation constants for the reaction VO(acac)$_2$ + Solv $\rightleftharpoons$ VO(acac)$_2\cdot$Solv.

Solvent	K/mol^{-1} dm^3 [a]	K/mol^{-1} dm^3 [b]	K/mol^{-1} dm^3 [c]
Py	52.6	34.4	
HMPA	58.8	22.7	
DMSO	6.25	4.55	3.8 ± 0.5
DEA		4.91	
DMA		3.26	2.0 ± 0.5
DMF	2.44	2.56	1.9 ± 0.5
TMP	0.769	0.833	
MeOH			0.43 ± 0.003
THF			0.30 ± 0.003
Dioxane			0.086 ± 0.003
AC			0.069 ± 0.003
EtOAc			0.052 ± 0.003
An			0.047 ± 0.002
PN			0.034 ± 0.001

[a] From spectroscopic titration in An from ref. 9.

[b] From spectroscopic titration in CH_2Cl_2 from ref. 9 except the values for DMA and DEA, which are taken from ref. 33.

[c] From Far IR spectra in bulk solvent (present work).

Downloaded At: 17:38 23 January 2011

Downloaded At: 17:38 23 January 2011

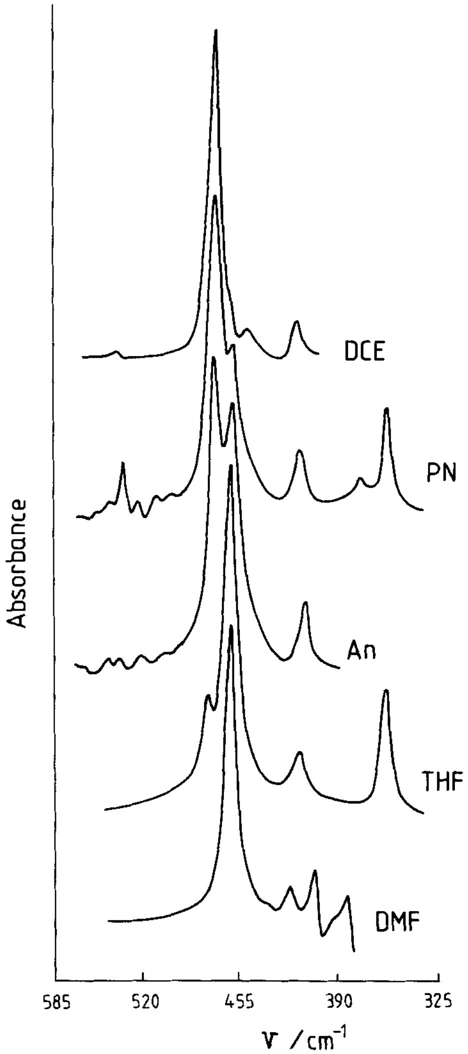


FIGURE 3 Splitting of the peaks found in the Far IR region of 330–580 cm^{-1}.

Here, α is the O=V–O angle, γ the angle between the two planes including the vanadium atom and the pair of oxygen atoms belonging to an acetylacetonate molecule and β the O–V–O bonding angle with an acac$^-$-moiety, which is assumed to have invariantly the same value as in the free solid VO(acac)$_2$, namely 88°. It can be expected[6] that the VO_4 fragment opens umbrella-like upon coordination of a donor molecule. Table VI collects the observed I_{B2}/I_{A1} ratios and the obtained angles γ. Due to the rather low intensity of the A_1 band overlapping with the intense band originating from the $\nu_{VO_4}(B_1)$ vibration these values might vary up to ±5° for strong donors. For free VO(acac)$_2$ a value of 133.2° is found. This corresponds to a O=V–O angle of 106.8° which is in good agreement with the value obtained by

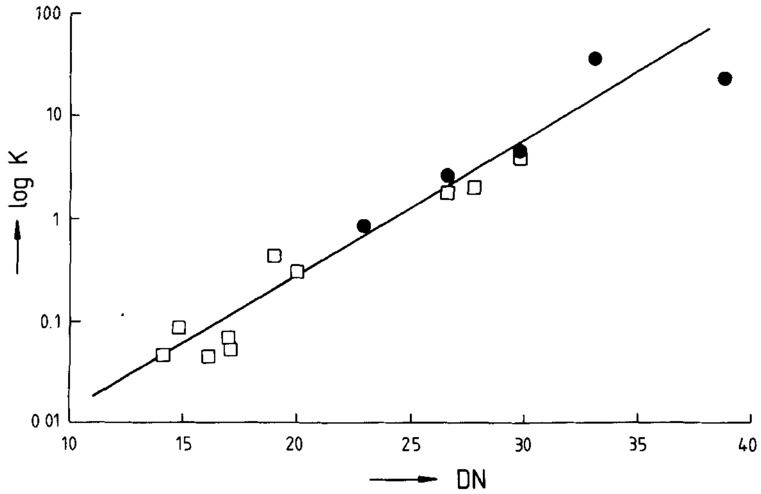


FIGURE 4 Dependence of the association constants of the reaction $VO(acac)_2 + Solv \rightarrow VO(acac)_2 \cdot Solv$ on the donor number of the solvent. ●: from Ref. 9; □: this work.

Downloaded At: 17:38 23 January 2011

TABLE VI
Far IR intensity ratios I_{B_2}/I_{B_1} angles between the vanadium-acetylacetonate planes (γ) and O=V–O angles (α) for $VO(acac)_2$ in solution and in the solid state.

	I_{B_2}/I_{B_1}	γ/°	α/°
	Solution		
1,2-Dichloroethane	3.2	121.6	110.5
Benzene	2.8	118.3	111.7
Nitromethane	3.6	124.7	109.5
Nitrobenzene	4.5	129.5	107.9
Bromobenzene	4.7	130.5	107.5
Acetonitrile	5.0	131.8	107.1
Propionitrile	6.1	135.8	105.7
Acetone	8.0	141.1	103.9
Ethylacetate	7.0	138.6	104.7
Methanol	6.7	137.7	105.0
Tetrahydrofurane	10.3	145.4	102.4
N,*N*-Dimethylformamide	8.8	142.7	103.3
Pyridine	11.0	147.3	101.7
	Solid state		
Free $VO(acac)_2$	5.2	132.6	106.8
N,*N*-Dimethylformamide	17.7	153.2	99.6
N,*N*-Dimethylacetamide	17.0	152.7	99.8
Dimethylsulfoxide	15.3	151.4	100.3
Pyridine	18.0	153.5	99.5

X-ray diffraction[34] of 106°. Figure 5 shows that γ increases with increasing DN of the solvent, as expected. In the solid state the angles between the two $acac^-$ planes are generally larger than in solution. The value of γ for the solid pyridine adduct is 153.5°, corresponding to a O=V–O angle of 99.5° and is in good agreement with the value obtained from X-ray diffraction[35] of $\gamma = 159.5°$.

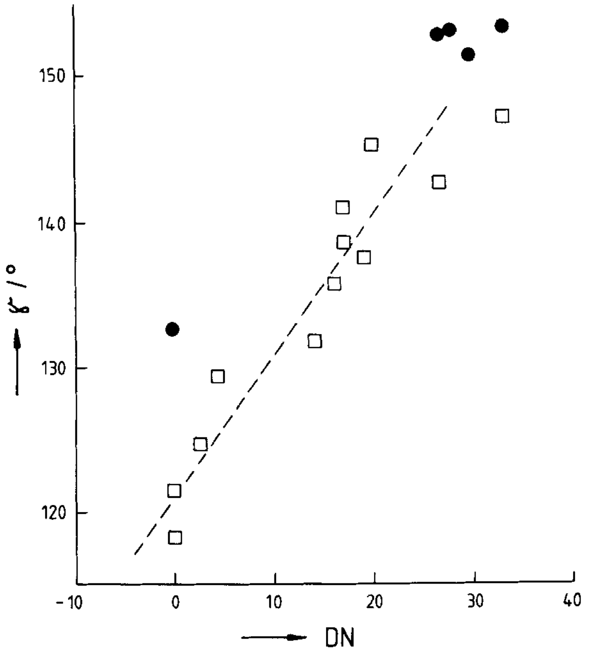


FIGURE 5 Calculated angles between the two vanadium-acetylacetonate planes *versus* donor number (γ); ● = solid state; □ = solution.

Downloaded At: 17:38 23 January 2011

Electrochemical Investigations

Figure 6 shows as a representative example a cyclic voltamogram of $VO(acac)_2$ in acetone. Peaks 1 and 5 can be assigned to the reduction of coordinated acetylacetonate as described earlier.[36,37] This process is found to be irreversible and depends upon the concentration of free acetylacetone but is rather independent of the solvent donor number.

The most stable oxidation state in An is V(III)[38,39] indicated by the comproportionation of V(II) and $VO(acac)_2$. Peaks 2 and 4 can be assigned as a reduction of vanadium(IV) to vanadium(III) according to (*4*)

$$VO(acac)_2 + e^- + Hacac \rightleftharpoons V(acac)_3 + OH^- \qquad (4)$$

This process is found to be slightly irreversible but becomes reversible with addition of an excess of acetylacetone. In solvents of higher donor number, peak 2, being associated with the reverse of reaction (*4*), becomes split into two peaks.[38,39] This can be interpreted by coordination of a (strong) solvent donor molecule instead of the $acac^-$ moiety. Under addition of excess acetylacetone, only one peak appears (as in solvents with lower DN). However, without excess Hacac a rather complex electrochemistry occurs especially in solvents of low donor number.[38,39] In the presence of excess acetylacetone the (reversible) redox potentials (measured *versus* bisbiphenylchronium(I)tetraphenyloborate) are found to be linearly shifted towards more positive values with increasing donor number of the solvent (see Fig. 7). This reflects increasing stabilities of the $VO(acac)_2$ solvates with increasing donor number and is in agreement with earlier findings.

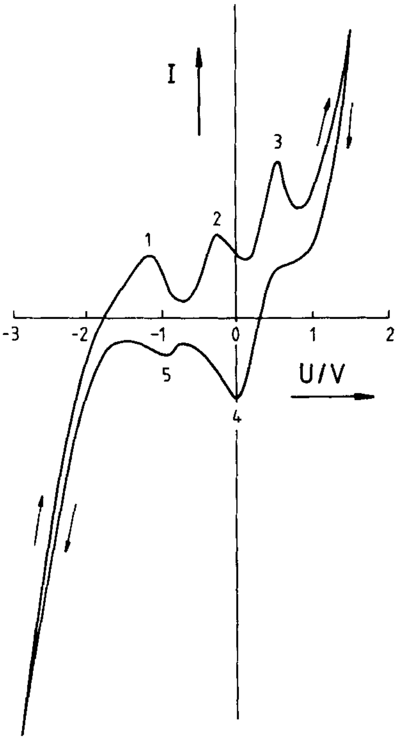


FIGURE 6 Cyclic voltamogram of 10 mM $VO(acac)_2$ in acetone (0.1 M /NBu_4][BPh_4] on the platinum electrode *versus* BBCr (scan rate 200 mV s^{-1}).

Downloaded At: 17:38 23 January 2011

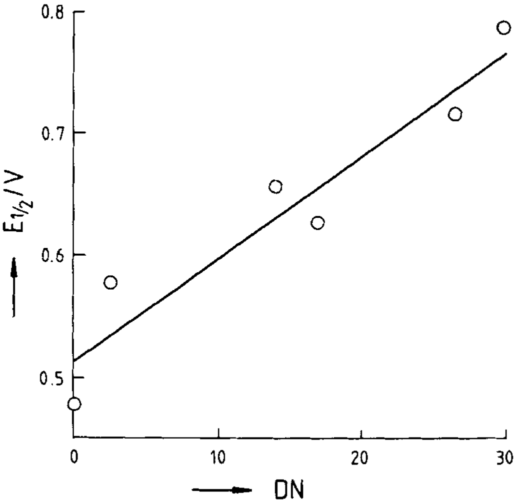


FIGURE 7 Donor numbers *versus* the redox potentials of 10 mM $VO(acac)_2$ in different solvents (0.1 M [NBu_4][BPh_4] with a five-fold excess of acetylacetone measured with cyclic voltametry *versus* BBCr.

Downloaded At: 17:38 23 January 2011

TABLE VII

Results from relativistic INDO calculations. Minimal energy (E_{min}) are given in eV, distances (d) in Å, charges (q) in elementary units.

Species	E_{min}	d(V=O)	d(V=O)	d(V—D)[a]	α/°[b]	B(V=O)[c]	B(V—O)[d]	q(V)	q(O)[e]	q(O)[f]
$^2[VO(acac)_2]$	−4548.48	1.56	1.98		106.0[g]	2.50	0.719	0.20	−0.26	−0.28
$^2[VO(acac)_2 \cdot An]$	−5278.77	1.56	2.00	2.4	101	2.47	0.643	0.15	−0.28	−0.27
$^2[VO(acac)_2 \cdot DMSO]$	−5770.08	1.56	2.00	2.4	101	2.46	0.646	0.21	−0.29	−0.31
$^2[VO(acac)_2 \cdot Cl^-]$[h]	−5414.50	1.56	2.00	2.6	101	2.33	0.560	0.23	−0.43	−0.32
$^1[VO(OH_2)_5]^+$	−3010.47	1.57	2.37	2.37	90	2.52	0.399	0.02	−0.30	−0.27
$^2[VO(OH_2)_5]^{2+}$	−3002.43	1.52	2.30	2.30	95	2.76	0.476	0.44	−0.03	−0.26

[a] Optimized bond distance between V and the donor atom of a coordinated solvent.

[b] Optimized bond O=V–O angle.

[c] Bond index of the V=O bond.

[d] Bond index of the V–O_{acac} bond (mean value of all O_{acac}).

[e] Charge at the vanadyl-oxygen.

[f] Charge at acac-oxygen.

[g] Taken from X-ray diffraction data.[34]

[h] Charge at Cl^-: −0.59.

The peak 3 in Figure 6 refers to the irreversible oxidation of vanadium(IV) to vanadium(V), yielding probably a VO_2^+ species. Again, this peak is strongly influenced by the donor properties of the solvent. However, it refers to an irreversible process which does not contain thermodynamic information of a simple kind.

Quasi-relativistic INDO calculations

The $VO(acac)_2$ as well as the $VO(acac)_2 \cdot Solv$ systems are electronically similar to $VO(H_2O)_5^{2+}$ (also calculated for comparison). With the exception of $VO(H_2O)_5^+$, all calculated compounds have a spin multiplicity of 2. One unpaired d electron is positioned at a d_{xy} orbital. A comparison of the occupation of α- and β-spin orbitals shows that this electron is excited in optical spectroscopy. The same orbital is responsible for both one-electron oxidation and one-electron reduction processes. This explains the relatively weak dependence of the d–d transition spectra and of the redox-potentials on the donor properties of a coordinated solvent molecule, because such coordination does not involve directly the vanadium d_{xy}-orbital.

Table VII collects some results of the *quasi*-relativistic INDO-calculations. The bond angles and distances are obtained from geometry optimization yielding the respective minimum for the total energy. They exhibit only small variations with changing donor strength of a coordinate solvent or a coordinated Cl^- anion. However, changes due to change in the coordination number as well as replacement of the acetylacetonate ligands by aqua ligands lead to significant changes in the V=O, the V–O and the $\alpha_{O=V-O}$ values. The O=V–O bond angle of 101° for the An, DMSO and the Cl^- adducts fit to the angles found for the solid solvates. These findings are in agreement with the so-called bond angle variation rule.[40] As mentioned above, the experimental angles found in solutions are larger, so that it might be argued that electrostatic dipole interactions enlarge this angle by a decrease in the actual charge of the ligand atoms.

The bond indices (Wiberg indices) depend more sensitively upon the donor properties of the coordinated species. In agreement with the changes observed in the Far IR-spectra, the V=O bond (with a bond index of about 2.5) is much less influenced and more rigid than the $V-O_{acac}$ bond.

The vanadium coordination centre carries only about 0.2 elementary charges and this increases with increasing donor strength of the coordinated donor molecule. This agrees well with the expectations according to the so-called spill-over effect, whereas the respective pile-up effect is reflected at the O atoms.[30,40] Charges at the respective O atoms reflect a pronounced *trans*-influence leading to stronger charges at the vanadyl oxygen atom compared to the acetylacetonate oxygen atoms which are positioned in the plane perpendicular to the attack of the donor. The relatively low negative charge at the vanadyl oxygen atom may have its origin in the high bond order of 2.5.

ACKNOWLEDGEMENTS

Thanks are due to the "Fonds zur Förderung der wissenschaftlichen Forschung" (Project 7605 and 8795) for financial support of this work.

Downloaded At: 17:38 23 January 2011

REFERENCES

1. K. Sone and Y. Fukuda, "Inorganic Thermochromism", Inorganic Chemistry Concepts, Vol. 10 (Springer, Berlin, 1987).
2. I. Bernal and P. H. Rieger, *Inorg. Chem.*, **2**, 256 (1963).
3. J. Selbin, *Chem. Rev.*, **65**, 153 (1965).
4. A. Taha, V. Gutmann and W. Linert, *Monatsh. Chem.*, **122**, 327 (1991).
5. W. Linert, B. Pouresmaeil, V. Gutmann, K. Mafune, Y. Fukuda and K. Sone, *Monatsh. Chem.*, **121**, 765 (1990).
6. W. Linert, A. Sotriffer and V. Gutmann, *J. Coord. Chem.*, **22**, 21 (1990).
7. W. Linert, V. Gutmann and A. Sotriffer, *Vibr. Spectr.*, **1**, 199 (1990).
8. R. N. Rowe and G. E. Pake, *Inorg. Synth.*, **5**, 115 (1957).
9. V. Gutmann and U. Mayer, *Monatsh. Chem.*, **99**, 1383 (1968).
10. M. R. Caira, J. M. Haigh and L. R. Nassimbeni, *J. Inorg. Nucl. Chem.*, **34**, 3171 (1972).
11. A. Rosenheim and H. Y. Mong, *Z. Anorg. Chem.*, **148**, 34 (1925).
12. J. S. Jaworski, *Electrochim. Acta*, **31**, 85 (1986).
13. W. Linert and J. S. Jaworski, *Electrochim. Acta*, **33**, 1713 (1988).
14. G. Gritzner, *Inorg. Chim. Acta*, **24**, 5 (1977).
15. R. Boca, Program MOSEM7, Slovak Technical University, Bratislava (1988), unpublished.
16. R. Boca, *Int. J. Quantum Chem.*, **31**, 941 (1987).
17. R. Boca, *Int. J. Quantum Chem.*, **37**, 209 (1990).
18. R. Boca, *Int. J. Quantum Chem.*, **34**, 385 (1988).
19. R. Boca, *Czech. J. Phys.*, **B40**, 629 (1990).
20. R. Boca, *Int. J. Quantum Chem.*, **33**, 159 (1988).
21. C. P. Stewart and A. L. Porte, *J. Chem. Soc., Dalton Trans.*, 1661 (1992).
22. T. R. Ortolano, J. Selbin and S. P. McGlynn, *J. Chem. Phys.*, **41**, 262 (1964).
23. E. M. Nour, A. N. Alnaimi and A. B. Alsada, *J. Phys. Chem. Solids*, **51**, 907 (1990).
24. J. P. Wilshire and D. T. Sawyer, *J. Am. Chem. Soc.*, **100**, 3972 (1978).
25. S. R. Cooper, Yu. B. Koh and K. N. Raymond, *J. Am. Chem. Soc.*, **104**, 5092 (1982).
26. J. Selbin, G. Maus and D. L. Johnson, *J. Inorg. Nucl. Chem.*, **29**, 1735 (1967).
27. J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, **26**, 37 (1964).
28. C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
29. K. Dichmann, G. Hamer, S. C. Nyburg and W. F. Reynolds, *Chem. Comm.*, 1295 (1970).
30. V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions" (Plenum Press, New York, 1978).
31. B. A. Vickova, B. Strauch and M. Horak, *Coll. Czech. Chem. Comm.*, **52**, 686 (1987).
32. W. Beck, A. Melnikoff and R. Stahl, *Chem. Ber.*, **99**, 3721 (1966).
33. E. Kwiatowski and J. Trojanowski, *J. Inorg. Nucl. Chem.*, **37**, 979 (1973).
34. R. P. Dodge, D. H. Templeton and A. Zalkin, *J. Chem. Phys.*, **35**, 55 (1961).
35. M. Shao, L. Wang and Y. Tang, *Kexue Tongbao* (*Foreign Language Ed.*), **29**, 759 (1984).
36. W. Linert, B. Pouresmaeil and V. Gutmann, *J. Coord. Chem.*, **17**, 15 (1988).
37. W. Linert, R. F. Jameson, V. Gutmann and B. Pouresmaeil, *J. Coord. Chem.*, **24**, 137 (1991).
38. M. Kitamura, K. Yamashita and H. Imai, *Bull. Chem. Soc. Jap.*, **49**, 97 (1976).
39. M. Kitamura, K. Sasaki and H. Imai, *Bull. Chem. Soc. Jap.*, **50**, 3199 (1977).
40. W. Linert and V. Gutmann, *Revs. Coord. Chem.*, submitted for publication.

Downloaded At: 17:38 23 January 2011