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Reactions of Metal β-Diketonates. IV. Reactions of Bis(acetylacetonato)-oxovanadium(IV) Hydrate, $VO(acac)_2H_2O$, with Chelating Ligands

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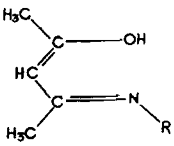
The reactions of bis(acetylacetonato)oxovanadium (IV) hydrate, $VO(acac)_2H_2O$, with different chelating ligands (containing at least one NH_2 group) have been studied. In dry refluxing toluene, heterochelates of the type $[VO(acac)(L{-}L)]^{0\,(\text{or}+)}\cdot nH_2O$ (where L–L = neutral or monoanion of bidentate chelating ligands; n = 0–1) have been isolated. On the other hand, dibasic tridentate (LH_2) or dibasic tetradentate ($L'H_2$) Schiff bases replaced all the acetylacetonate anions from $VO(acac)_2H_2O$ to produce $VO(L)H_2O$ or $VO(L')$ in refluxing toluene or ethanol. Analogous reactions of $VO(acac)_2H_2O$ with aminoacids, amino-alcohols, semi- and thiosemi-carbazide in ethanol, methanol, water–ethanol or water–acetone mixture, produced a variety of mixed ligand complexes of oxovanadium(IV) ion involving Schiff bases, many of which show subnormal magnetic moments at room temperature. In the course of this study several mixed ligand oxovanadium(IV) complexes with neutral acetylacetone (or glycine) have also been isolated. The reactions of $VO(acac)_2H_2O$ with chelating amino ligands in presence of even trace amount of water invariably result in the template syntheses of Schiff base chelates, which has been discussed qualitatively.

The electronic spectra of these chelates have been interpreted with the help of either C_{2v} or C_{4v} local symmetry. The elemental analyses, i.r. spectral data and cryomagnetic data have also been used to characterise the complexes.

Introduction

Bis(acetylacetonato)metal(II), $M^{II}(acac)_2$, may behave as Lewis acids and react with nitrogen bases to form 1:1 or 1:2 addition compounds [1]. Corresponding reactions of $M^{II}(acac)_2$ with chelating ligands are also known [2–10], although extensive studies are yet to be made. Reactions of $VO(acac)_2H_2O$ with different chelating amino ligands have never been studied. Herein, we report the reactions of $VO(acac)_2H_2O$ (A) with ethylenediamine (en), ethanolamine (ena-H), glycine (gly-H), orthoaminophenol (oap-H), anthranilic acid (aa-H), semicarbazide (sc-H), and thiosemicarbazide (tsc-H). This paper also describes the reactions of (A) with Schiff bases N-phenylsalicylaldimine (SAN-H), N(2hydroxy)-phenylsalicylaldimine (SOAP-H_2), N-(2-hydroxy)-ethylsalicylaldimine (SALENA-H_2) and NN′-ethylenebis(salicylaldimine) (SALEN-H_2).

The following abbreviations have been used for the Schiff bases of acetylacetone:



ACENA-H_2 (R = CH_2CH_2OH), ACGLY-H_2 (R = CH_2COOH), ACTSC-H_2 (R = $NHCSNH_2$), ACSC-H_2 (R = $NHCONH_2$), ACOAP-H_2 (R = o-C_6H_4OH), and ACAA-H_2 (R = o-C_6H_4COOH).

Experimental

Elemental analyses of V and N were done in the laboratory by conventional methods. The microanalyses of C and H of some of the samples were done by the Central Drug Research Institute, Lucknow. Infrared spectra (KBr phase) were measured by the same Institute. Conductances were measured with a Mullard conductivity bridge. Electronic spectra were recorded in Beckman DU-2 or Spectromom spectrophotometers. Magnetic susceptibilities were recorded in a Gouy balance by usual methods. Molecular weights were determined in benzene or chloroform cryoscopically. Solvents and chemicals were purified and dried by usual procedures.

Reactions of $VO(acac)_2H_2O$

The following general method was used to carry out the reactions of the title complex with different chelating ligands.

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TABLE I. Elemental Analyses, Magnetic Moments, Colours and Melting Points of Some Oxovanadium(IV) Complexes.

Complex	Colour	M.P. (°C)	% Found[a]		% Calc.		μ_{eff} B.M.
			V	N	V	N	(Temp.)
$[VO(ACENA)H_2O]_2$, (I)	Blue	>300°	23.00	6.60	22.57	6.20	0.95(22.0 °C)
$[VO(acac)(ena)H_2O]$, (II)	Dark Green	–	20.15	5.52	20.90	5.73	1.78(27°C)
$[VO(ACOAP)(acac\text{-}H)]H_2O$, (III)	Deep Snuff	180–185° (dec.)	13.06	4.20	13.65	3.74	1.65(21°C)
$[VO(acac)(oap)H_2O]$, (IV)	Brown	240–245°	17.47	4.79	17.47	4.79	1.71(27°C)
$[VO(ACAA)(acac\text{-}H)H_2O]H_2O$, (V)	Grey	158–160°	12.74	3.20	12.69	3.48	1.67(21°C)
$[VO(acac)(aa)H_2O]$, (VI)	Light Brown	>300°C	16.58	4.11	16.78	4.60	1.73(28°C)
$[VO(ACGLY)(gly\text{-}H)]_2 \cdot 6H_2O$, (VII)	Green	230–235° (dec.)	14.06	7.90	14.74	8.12	1.10(21°C)
$[VO(acac)(ACTSC\text{-}Na)]H_2O^b$, (VIII)	Greenish Grey	>300°	14.08	11.67	13.46	11.09	1.77(26°C)
$[VO(acac)(ACSC\text{-}Na)]^b$, (IX)	Green	>300°	14.40	12.82	14.82	12.21	1.66(21°C)
$[VO(acac)OH]_2en$, (X)	Green	~300°	23.80	6.34	23.94	6.57	1.49(26.5°C)
$[VO(acac)(SAN)H_2O]$, (XI)	Yellow	118–120°	13.13	3.47	13.42	3.68	1.76(23°C)
$[VO(SOAP)H_2O]$, (XII)	Brown	>300°	17.22	4.99	17.23	4.73	1.78 (22°C)
$[VO(SALEN)]$, (XIII)	Green	295–8° (dec.)	15.58	8.85	15.32	8.41	1.71(28°C)
$[VO(SALENA)H_2O]$, (XIV)	Dark Violet	>300°	20.92	5.64	20.56	5.64	1.68(30°C)
$[VO(acac)OH]_2ena\text{-}II$, (XV)	Snuff	236–238°	23.12	3.33	23.89	3.28	1.02(30°C)
$[VO(SALENA)H_2O]_2$, (XVI)	Brown	>300°	20.75	5.55	20.56	5.64	1.52(29.5°C)
$VO(acac)_2$	–	–	–	–	–	–	1.73(25°C)

[a] Elemental analyses of C and H of these complexes are in conformity with the formulations. [b] Satisfactory analyses for S and Na have been obtained. [c] Satisfactory analysis for Na has been obtained.

An equimolar (0.01 mol) mixture of $VO(acac)_2H_2O$ [11] and the chelating ligands in toluene, dichloromethane, ethanol, methanol, acetone–water or ethanol–water mixtures was refluxed for 1–3 hr. Sometimes crystals were obtained during reflux, and in other cases the solid complexes were isolated from the refluxed solutions after suitable treatment. The compounds were purified either by recrystallization from suitable solvents, or by thorough washing with solvents.

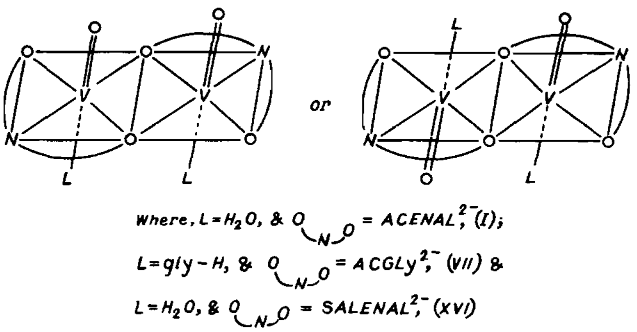
Results and Discussion

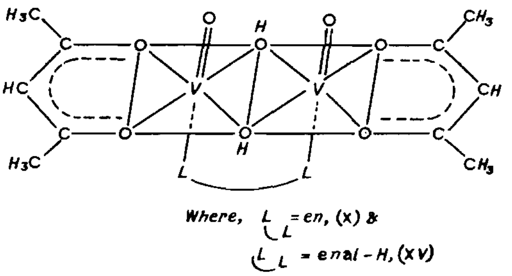
Reactions of $VO(acac)_2H_2O$ (A) with many chelating amino ligands have been studied in different solvents and a variety of mixed ligand complexes of oxovanadium(IV) have been isolated in the solid state as shown in Table I. Excepting the two complexes XII and XIII of Table I, all other vanadyl complexes reported in this communication are new. The complxes are all coloured and stable in atmospheric conditions. Elemental analyses support their formulations. Molecular weights of some of these complexes have been measured (Table IV), and found to be in conformity with their formulations.

They are all paramagnetic (Table I), and the complexes II to VI, VIII, IX, and XI to XIV show μ_{eff} values in the range 1.66 to 1.78 B.M., which are quite close to the spin-only value for one unpaired electron as is expected for oxovanadium(IV) chelates. These approximately normal magnetic moment values indicate that there are no significant interactions between neighbouring vanadium ions. On the other hand, complexes I, VII, X, XV and XVI show subnormal magnetic moments (μ_{eff} in the range 0.95 to 1.52 B.M.). These lower μ_{eff} values may be compared with the subnormal magnetic moment values (~ 0.77 to 1.55 B.M.) reported by Zelentsov [12] for vanadyl complexes of N-(*o*-hydroxyphenyl)-salicylidineimine ligands. The d^1 configuration of oxovanadium(IV) suggests a spin-coupling phenomenon as was observed in many copper(II) complexes of tridentate Schiff bases [13, 14]. The exact mechanism for spin-exchange is, however, controversial [14, 15]. Zelentsov suggested the same arising from antiferromagnetic exchange coupling between pairs of vanadyl ions; the molecular orbital considerations [16] and ESR studies [17] also reveal that the direct spin-exchange between two vanadium atoms is not unlikely, and that the spin-coupling *via* the bridging oxygen atoms may not be the dominant exchange mechanism in vanadium(IV) complexes although it was suggested for many copper(II) complexes of tridentate Schiff bases [14, 18]. However, the following tentative structures may be proposed for the oxovanadium(IV) complexes with subnormal magnetic moments:

TABLE II. Electronic Absorption Spectral Bands (cm^{-1}, nujol mull) for Some Subnormal Oxovanadium(IV) Complexes.

Complex	μ_{eff} (B.M.)	Band I	Band II	Band III	Band IV
$[VO(ACENA)H_2O]_2$, (I)	0.95	14,925	17,000(sh)	21,275	27,500
$[VO(ACGLY)(gly\text{-}H)]_2 \cdot 6H_2O$, (VII)	1.10	13,000(sh)	15,400(sh)	21,300	27,000
$[VO(acac)(OH)]_2en$, (X)	1.49	13,500(sh)	16,950(sh)	–	30,000
$[VO(acac)OH]_2enol\text{-}H$, (XV)	1.02	13,000(sh)	17,000(sh)	24,400	–
$[VO(SALENA)H_2O]_2$, (XVI)	1.52	14,500(sh)	16,800(sh)	19,200	27,000





The magnetic susceptibilities of the complexes I, VII and XVI have been measured at three different temperatures (Table V). The room temperature magnetic moments (Table I) decreased considerably as the temperature was lowered (Table V). The dependence of the magnetic susceptibilities on temperature is characteristic of antiferromagnetic exchange interaction.

The electronic spectra of the complexes with subnormal mangetic moments were measured in Nujol mulls. All the complexes studied exhibit several bands (about four bands) around 13,000–14,500 cm^{-1}, 15,500–17,000 cm^{-1}, 18,000–20,000 cm^{-1}, and 21,000–30,000 cm^{-1} (Table II). If we classify these bands as band I, II, III and IV, then in most cases bands III and IV are well developed. The two other bands (*i.e.* bands I and II) are not well developed in many cases and appear as shoulders. Spectral bands in other subnormal VO(ONO) and VO(ONS) complexes also appear as shoulders [19]. The spectral bands are assigned according to the Vanquickenborne and McGlynn (V–M) scheme [20] for oxovanadium(IV) complexes. They have proposed the following ordering of vanadium *d* orbitals: $d_{xy} < d_{xz}, d_{yz} < d_{x^2-y^2} < d_{z^2}$. According to the V–M scheme band I and band II are assigned to the $d_{xy} \rightarrow d_{xz}, d_{yz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. It seems interesting to compare the electronic spectra of the present oxovanadium(IV) complexes with subnormal magnetic moments with the spectra of normal oxovanadium(IV) complexes [21], *viz.*, $VO(salicylaldimine)_2$ (see later discussion of electronic spectra of the present oxovanadium(IV) complexes with normal magnetic moments). The positions of the bands in these two series of complexes do not differ appreciably. The appearance of undeveloped bands is possibly the characteristic of electronic spectra of the subnormal oxovanadium(IV) complexes (*loc. cit.*).

The electronic spectra along with their tentative assignments (on the basis of C_{2v} local symmetry) [22–25] of present oxovanadium(IV) complexes with normal magnetic moments are given in Table III. In many cases the bands are not well resolved, and appear either as very broad bands or as shoulders.

Infrared spectra of some of these oxovanadium complexes are measured in KBr phase and the representative i.r. bands for $\nu_{V=O}$ of some of these chelates have been included in Table IV. The presence of monomeric V=O unit in normal oxovanadium(IV) heterochelates is revealed in the infrared spectral data for the V=O stretch [26] which occurs in the range 955 to 983 cm^{-1}. These values are slightly lower than the value observed (996 cm^{-1}) for $\nu_{V=O}$ in $VO(acac)_2$. The slight decrease in V=O stretches of the present mixed ligand chelates may be due to the stronger ligand fields of these ligand systems, which lower the V=O stretching vibrations.

In the infrared spectra of the subnormal complexes the characteristic V=O stretching frequencies were found in the region 965–900 cm^{-1} (Table IV). These bands are usually very strong and broad, and in some cases are split into two bands. The splitting of the V=O band may be due to unit cell group splitting or to a crystal-packing effect [27].

All the vanadyl complexes containing the coordinated 'acac' anion under investigation show bands in the range 1550 to 1500 cm^{-1} which are attributed to the C=O and C=C stretchings of the chelated

TABLE III. Electronic Absorption Spectral Bands (cm^{-1}) for Some Normal Oxovanadium(IV) Complexes.

Complex	Solvent	Band (logϵ)	Tentative assignments		
			Band III $b_2 \to {}^1a_1^*$ ${}^2B_2 \to {}^2A_1$	Band II $b_2 \to b_1^*$ ${}^2B_2 \to {}^2B_2$	Band I $b_2 \to e^*$ ${}^2B_2 \to {}^2E$
VO(acac)(ena)H_2O	EtOH	38,400(sh) 31,250(sh)	25,600(sh)	16,940(1.32)	12,980(1.25)
VO(acac)(oap)H_2O	EtOH	40,820(sh) 37,030(4.26)	23,260(3.45)	20,000(sh)	15,880(sh)
VO(acac)(SAN)	$CHCl_3$	40,820(sh) 36,370(3.64) 33,340(sh)	29,416(sh)	17,240(1.33)	15,380(1.29)
VO(SOAP)H_2O	$CHCl_3$	40,000(3.98) 33,900(3.20) 28,170(sh)	24,000(sh)	19,610(sh)	–
VO(acac)(ACSC-Na)	H_2O	42,550(4.18) 38,460(sh)	–	20,410(sh)	15,880(sh)
VO(acac)(ACTSC-Na)H_2O	H_2O	38,460(sh) 31,250(sh)	–	20,500(sh)	15,630(sh)
VO(SALENA)H_2O	$CHCl_3$	38,400(3.95)	27,780(3.58)	19 230(1.63)	–

TABLE IV. V=O Stretching Frequencies of Some Oxovanadium(IV) Complexes.

Complex	$\nu_{V=O}$ (cm^{-1})	Molecular Weight[a]
VO(acac)$_2$	996	–
[VO(ACENA)H_2O]$_2$, (I)	980	235(226)
VO(acac)(ena)H_2O, (II)	978	259(244)
VO(ACOAP)(acac-H)H_2O, III	981	401(374)
VO(acac)(oap)H_2O, (IV)	983	
VO(acac)(aa)2H_2O, (VI)	983	
VO(acac)(ACTSC-Na)H_2O, (VIII)	960	
[VO(acac)OH]$_2$en, (X)	965	
VO(acac)(SAN)H_2O, (XI)	955	368(380)
VO(SOAP)H_2O, (XII)	1000	
VO(SALENA)H_2O, (XIV)	995	215(248)
[VO(SALENA)H_2O]$_2$, (XVI)	990	

[a] Calculated values are given in parentheses.

TABLE V. Magnetic Moments at Various Temperatures of Some Oxovanadium(IV) Complexes.

Complex		Temperature °K		
		295	260	190
[VO(ACENA)H_2O]$_2$ (I)	μ_{eff} B.M.	0.95	0.82	0.60
[VO(ACGLY)(gly-H)]$_2 \cdot 6H_2O$ (VII)	μ_{eff} B.M.	1.10	1.00	0.92
[VO(SALENA)H_2O]$_2$ (XVI)	μ_{eff} B.M.	1.52	1.38	1.29

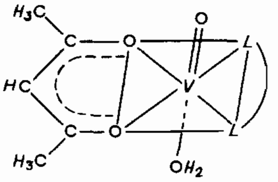
acetylacetonate group [28]. On the other hand, the complexes III and V show the carbonyl stretching absorption at about 1700 cm^{-1} indicating the involvement of the ketonic molecule of acetylacetone [29]. The $\nu_{C=N}$ in the Schiff base complexes are observed around 1630 to 1580 cm^{-1} and are about 10 to 30 cm^{-1} lower than the $\nu_{C=N}$ of free Schiff bases. This demonstrates the coordination of imine N atom.

The complexes I, II, IV, V, VI, XI, XII, XIV and XVI exhibit a broad water absorption with medium or weak intensity centered about 3400–3300 cm^{-1}. Free water has two stretching modes at 3650 and 3560 cm^{-1} while coordinated water absorbs [30] at 3095 and 3059 cm^{-1}. The lowering of the water stretching modes to 3400–3300 cm^{-1} suggests that water is not present in the compounds simply as water of hydration but rather as coordinated molecules. The appearance of another band near 750–850 cm^{-1} in these chelates further supports the presence of coordinated water molecules. Nevertheless, the complexes III, V, VII, VIII show several weak to medium bands in the range 3000–3500 cm^{-1}, which demonstrates the presence of lattice water molecules in these chelates. The ν_{NH} also appeared in this region in the complexes VIII and IX, both of which are highly soluble in water. All these support the tentative structural assignments shown in the last formula although the nature of H_2O molecule is not definitely known from present data.

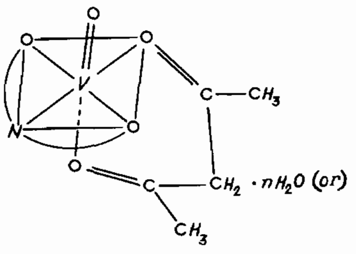
The complex VII shows a strong band at 1715 cm^{-1}, which may be considered as the un-ionized COO stretching band [31]. Unidentate glycine exhibits band at 1610 cm^{-1} for ionized COO stretching in [Pt(gly)$_2$(NH$_3$)$_2$], while the same stretching band for un-ionized unidentate glycine in [Pt(gly H)$_2$Cl$_2$] appears at 1710 cm^{-1} [31]. However, the interpretation of the present i.r. data is purely qualitative, and the assignments are tentative. Besides the characteristic i.r. absorption bands for chelated acetylacetonate and OH$^-$ ions (as discussed above), the complex X shows characteristic bands for bridging ethylenediamine [32]. The bands observed at 1550, 1340, 1200 and 670 cm^{-1} may be assigned as δNH$_2$ (scissors, wag, twist and rock respectively). However, the δNH$_2$ (scissors) is difficult to assign in this complex due to the presence of chelated acetylacetonate ion (see above). Another set of four bands is observed at 1448, 1370, 1285 and 765 cm^{-1}, and is assignable to δCH$_2$ scissors, wag, twist and rock respectively [32].

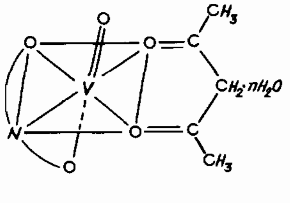
Conclusion

Elemental analyses, magnetic moments, electronic and infrared spectra of the present oxovanadium(IV) complexes afford evidence for the structural assignments depicted earlier and for the following ones:

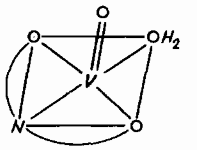


Where, (L L = enol⁻ (II); (L L = oap⁻ (IV); (L L = aa⁻ (VI); & (L L = SAN⁻ (XI)

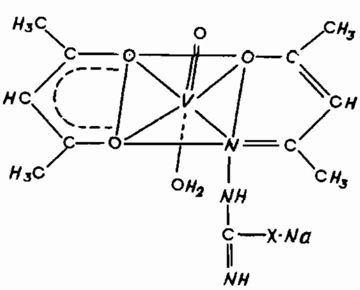




Where, O⌣N⌣O = ACOAP²⁻ (III); O⌣N⌣O = ACAA²⁻ (V)



Where, O⌣N⌣O = SOAP²⁻ (XII); & O⌣N⌣O = SALENOL²⁻ (XIV)



Where, X = S, (VIII); & X = O, (IX).

It has been observed in the present study that the reactions of VO(acac)$_2$H$_2$O with chelating amino ligands in dry refluxing toluene (or CH$_2$Cl$_2$) yielded mixed ligand complexes of oxovanadium(IV) ion with replacement of one acetylacetonate anion by the incoming chelating anion. No condensation of coordinated C=O group of 'acac' moiety has been observed. However, the same reactions, when performed in ethanol, methanol, aqueous acetone, or aqueous ethanol, yielded mixed ligand complexes of VO^{2+} involving the Schiff bases of acetylacetone and the incoming amino ligands. These template syntheses of Schiff base complexes may be rationalized as follows: (i) the water content of the solvent(s) may cleave one or both of the metal–carbonyl bonds present in VO(acac)$_2$, and the free end(s) of acetylacetone may condense with the chelating amino ligands to produce the Schiff base; (ii) VO(acac)$_2$ may form addition complexes with the incoming amino ligands (L–L) to form VO(acac)$_2$(L–L), in which the bonds of vanadyl ion with 'acac' may be weakened and thus help the condensation of C=O with the NH$_2$ group.

Similar template syntheses of Schiff base complexes of Cu(II), Co(II) and Ni(II) have been observed previously by us [8, 33], when M^{II}(acac)$_2$ reacted with different chelating amino ligands.

The complex I has been prepared by the reaction of (A) with ena-H in ethanol. This compound can also be prepared by the reaction of the pre-formed Schiff base with VO^{2+} in ethanol [34]. In the present study the complex XVI has been synthesized by the reaction of (A) with the Schiff base in toluene. In a previous study we have isolated the same complex by the reaction of the pre-formed Schiff base with VO^{2+} ion in ethanol. It has been further observed that the dibasic tridentate Schiff bases, LH$_2$, when reacted with (A) either in toluene or ethanol always yielded complexes of the type VO(L)·H$_2$O with normal magnetic moments; while the reactions of LH$_2$ with VO^{2+} ion in ethanol give [VO(L)]$_2$nH$_2$O with subnormal moments [34]. We could not isolate the complexes II, III, V, VII, VIII, and IX, with the pre-formed Schiff bases. Template synthesis, as observed in the present investigation, is thus the only route known for such heterochelates at present.

Acknowledgments

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