Indian Journal of Chemistry
Vol. 35A, June 1996, pp. 527-529

Water soluble mixed-ligand oxovanadium(IV) complexes of acetylacetone and aldimine ligands

Sankar Prasad Rath, Sujit Mondal & Tapas Ghosh*
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032

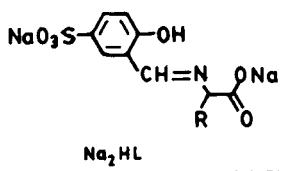
Received 21 June 1995; revised 18 December 1995

Water soluble mixed-ligand oxovanadium(IV) complexes of sulphonated salicylaldimine ligands of α-amino acids $Na_2HL.H_2O$[1, R = H, CH_3, $CH(CH_3)_2$ and CH_2Ph] and acetylacetone of the formula $Na_2[VO(L)(acac)].3H_2O$ have been synthesized and characterized by IR, UV/VIS, EPR, magnetic moments and redox behaviour. The coordination sphere of the complexes are of the type VO(ONO)(OO), where O atoms are phenolic, carboxylic, ketonic and enolic type and N is of azomethine type. The complexes are one electron paramagnetic and show 1:2 electrolytic conductivity. The complexes display irreversible one electron oxidation peaks in H_2O in the range 0.46-0.55 V vs SCE.

Tridentate ONO donor schiff bases derived from salicylaldehyde and amino acids have good affinity for oxovanadium (IV/V)[1-5]. The complexes are usually soluble in organic solvents but water soluble species are rare[6]. Herein we report a group of water soluble oxovanadium(IV) complexes incorporating the schiff base of sodium salicylaldehyde-5-sulphonate and α-amino acids. I (Na_2-HL, where H refers to dissociable phenolic proton). Acetylacetone (Hacac) is utilized as the coligand. Complexes of the type $Na_2[VO(L)(acac)].3H_2O$ have been isolated and characterized. Their spectra (IR, UV/VIS and EPR), conductance, magnetism and redox behaviour are discussed.

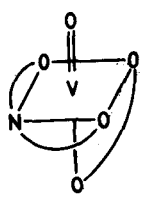
Experimental

Commercially available $VOSO_4.5H_2O$, salicylaldehyde, glycine, L(−), α-alanine, L(−)valine and L(−) phenylalanine were used as received. $[VO(acac)_2]$[7] and sodium salicylaldehyde-5-sulphonate monohydrate were prepared as reported[8]. All other chemicals and solvents were of AR grade and were used as such.



Na_2HL
R = H, CH_3, $CH(CH_3)_2$, CH_2Ph

(I)



(II)

Electronic spectra were recorded on a Hitachi 330 spectrophotometer, infrared spectra on a Perkin Elmer 783 spectrophotometer and EPR spectra in the X-band on varian E-109C spectrometer equipped with a quartz Dewar flask for low-temperature (77 K) measurements. For the measurement of room temperature EPR spectra in aqueous solution, a flat cell was used. Diphenylpicrylhydrazyl (dpph) ($g = 2.0037$) was used to calibrate the spectra. Magnetic susceptibilities were measured using a PAR model 155 Vibrating-Sample magnetometer fitted with Walker Scientific L75 FBAL magnet. Electrochemical measurements were performed on a PAR model, 370-4 electrochemistry system following the reported procedure[9]. All potentials reported in this work were uncorrected for junction contribution. Solution conductivities were measured with Systronics PR 304 bridge. A Perkin Elmer 240C elemental analyser was used for microanalytical data.

Synthesis of the ligands

The four schiff base ligands used in this work are of the type Na_2HL (I) containing different R groups [R = H, CH_3, $CH(CH_3)_2$ and CH_2Ph]. All the ligands were prepared by the same general method. Details are given for one representative case only.

Sodium N-5-sulphonato salicylidene glycinate monohydrate, $Na_2HL^1.H_2O$ (R = H)

To a methanolic (20 cm^3) solution of NaOH (256 mg, 6.4 mmol), glycine (480 mg, 6.4 mmol) was added while stirring at room temperature. Then 1.55 g (6.4 mmol) sodium salicylaldehyde-5-sulphonate monohydrate was added and the mixture stirred at room temperature. After 10 min, a canary yellow precipitate appeared which was filtered after stirring the mixture for another 1½ h, washed with cold methanol and dried over P_4O_{10} for 48 h. Yield: 71% [Found: C, 33.56; H, 2.78; N, 4.37; Reqd. for $C_9H_9O_7SNa_2$: C, 33.64; H, 2.80; N, 4.36%]. The yields with other amino acids are within the same range.

Table 1—Analytical and physical data of vanadium complexes

Complex (yield %)	Found (Calcd.) %			μ_{eff} (BM)	Λ_M $\Omega^{-1}cm^2mol^{-1}$	E^a_{pa}, V
	C	H	N			
$Na_2[VO(L^1)(acac)].3H_2O$ (85)	32.25(32.18)	3.68(3.64)	2.69(2.68)	1.66	218	0.55
$Na_2[VO(L^2)(acac)].3H_2O$(92)	33.52(33.58)	3.89(3.92)	2.60(2.61)	1.66	189	0.54
$Na_2[VO(L^3)(acac)].3H_2O$(89)	36.22(36.17)	4.40(4.43)	2.49(2.48)	1.69	190	0.53
$Na_2[VO(L^4)(acac)].3H_2O$(86)	41.22(41.18)	4.07(4.08)	2.29(2.29)	1.72	197	0.46

[a] In water: working electrode is platinum; reference electrode is SCE; supporting electrolyte is KCl.

Synthesis of the complexes

The four complexes reported in this work are of the type $Na_2[VO(L)(acac)].3H_2O$ and were prepared by the same general method. Details are given for one representative case only.

Sodium(acetylacetonato)(N-5-sulphonato salicylidene/glycinato)oxo-vanadium(IV)trihydrate, $Na_2[VO(L^1)(acac)].3H_2O$

To a methanolic (20 cm^3) suspension of $Na_2HL^1.H_2O$ (229 mg, 0.71 mmol), methanolic solution (10 cm^3) of $VO(acac)_2$ (210 mg, 0.79 mmol) was added dropwise with constant stirring at room temperature. After 20 min, a clear yellowish-green solution was obtained. After stirring the solution for another 2 h, the solvent was vacuum evaporated and then washed thoroughly with acetone and dried over P_4O_{10} for 24 h.

Results and discussion

Four sulphonated salicylaldimine ligands Na_2HL^1-Na_2HL^4 (general abbreviation Na_2HL) have been used in the present work. Acetylacetone (Hacac) is used as coligand. Upon treating a methanolic solution of $VO(acac)_2$ with an equimolar mixture of $Na_2HL.H_2O$, facile displacement of one $acac^-$ ion occurs with the incorporation of schiff base ligand forming a yellowish-green 1:2 electrolytic species. The reaction can be represented as follows:

$$VO(acac)_2 + Na_2HL \rightarrow Na_2[VO(L)(acac)] + acacH$$

The analytical and physical data are presented in Table 1. All the species display the expected solution conductivities[10] in water for 1:2 electrolyte and have magnetic moments corresponding to one unpaired electron.

The complexes display strong V=O frequencies in the region 940-955 cm^{-1} which is compatible with six-coordination[11,12]. The schiff base nature of the ligand is confirmed by the appearance of a band at 1630 cm^{-1} associated to C=N group. The band at 1650 cm^{-1} is characteristic of bonded CO_2^- moiety. The $\nu_{C=O}$ band of acetylacetone expected[13] near 1580 cm^{-1} could not be identified unambiguously due to the presence of other strong bands in the same region. The band at 540-570 cm^{-1} is assigned to V−O (aryl) and those at 440-450 cm^{-1} to the V−O(carboxyl)[14]. The broad water band in the region 3400-3500 cm^{-1} shows that there is no water coordinated to vanadium which should appear at longer wavelength.

Inspite of our best efforts, none of the complexes afforded crystals suitable for X-ray work. However, the meridional tridentate binding of α-amino acid schiff bases of salicylaldehyde have been documented in several instances by X-ray crystallography[3-5]. The bidentate binding of $acac^-$ to oxovanadium is also well established[15]. On the basis of above assumption, the most logical structure of the present family of complexes is as shown in Structure **II**.

All the complexes display two ligand field transitions[16], one at 820 and another in the region 550-560 nm. Strong absorptions at higher energies preclude observation of other possible ligand field transitions. A medium intensity band near 360 nm in the complexes corresponds to a $\pi \rightarrow \pi^*$ transition of salicylaldimine chromophore. All the complexes are EPR-active displaying characteristic eight-line pattern due to hyperfine splitting by ^{51}V (I=7/2) at room temperature (g_{av} = 1.971 and A_{av} = 99-100 G in water).

At 77 K in 1:2 water-ethylene glycol mixture, axially anisotropic spectra are observed with $g_\parallel < g_\perp$ and $A_\parallel \gg A_\perp$. Some of the pertinent values of EPR spectral data of $Na_2[VO(L)(acac)].3H_2O$ [where R = H, CH_3, $CH(CH_3)_2$ and CH_2Ph in L] complexes are for R = H: $g_\parallel(A_\parallel/G)$ 1.950 (176.6); $g_\perp(A_\perp/G)$ 1.982(62.4); $g_{av}(A_{av}/G)$ 1.971(100.5); for R = CH_3: $g_\parallel(A_\parallel/G)$ 1.950 (182.6); $g_\perp(A_\perp/G)$ 1.981 (62.1); $g_{av}(A_{av}/G)$ 1.971(102.3); for R = $CH(CH_3)_2$: $g_\perp(A_\perp/G)$ 1.953(183.6); $g_\perp(A_\perp/G)$ 1.981(64.0); $g_{av}(A_{av}/G)$

1.972(103.9); and for R = CH_2Ph : $g_{\|}(A_{\|}/G)$ 1.950 (181-0); $G_{\perp}(A_{\perp}/G)$ 1.980 (63.3); $g_{av}(A_{av}/G)$ 1.970 (102.5), where $g_{av} = 1/3\ [2g_{\perp} + g_{\|}]$ and $A_{av} = 1/3\ [2A_{\perp} + A_{\|}]$. This is usual for VO^{2+} complexes (axially compressed d^1_{xy} configuration)[15,17,18].

The redox behaviour of all the complexes was electrochemically examined in aqueous solution at Pt electrode. The complexes uniformly exhibit one-electron irreversible oxidation peak in water:

$[VO^{IV}(L)(acac)]^{2-} \longrightarrow [VO^{V}(L)(acac)]^{-} + e$. The oxovanadium(V) complexes so formed are unstable. The anodic peak potentials, E_{pa} are listed in Table 1. The E_{pa} values span in the range 0.46-0.55 V vs. SCE.

Acknowledgement

We are thankful to Prof. A Chakravorty for providing facilities and useful discussions. Financial support from the DST and CSIR, New Delhi, is acknowledged.

References

1 Theriot L J, Carlisle G O & Hu H J, *J inorg nucl Chem*, 31 (1969) 2841.
2 Hamalainen R & Turpeinen U, *Acta Crystallogr*, C41(1985) 1726.
3 Nakajima K, Kojima M, Toriumi K, Saito K & Fujita J, *Bull chem Soc Japan*, 62 (1989) 760.
4 Cavaco I, Pessoa J C, Cosa D, Duarte M T, Gillard R D & Matias P, *J chem Soc, Dalton Trans*, (1994) 149.
5 Mondal S, Dutta S & Chakravorty A, *J chem Soc, Dalton Trans*, (1995) 1115.
6 Evans D F & Missen P H, *J chem Soc, Dalton Trans*, (1987) 1279.
7 Rowe R A & Jones M M, *Inorg Synth*, 5 (1957) 113.
8 Botsivali M, Evans D F, Missen P H & Upton M W, *J chem Soc, Dalton Trans*, (1985) 1147.
9 Chandra S K, Basu P, Ray D, Pal S & Chakravorty A, *Inorg Chem*, 29 (1990) 2423.
10 Dutta R L, *Inorganic Chemistry—Part II : Chemical Elements & their compounds* (The New Book Stall, Calcutta) 1981, p 385.
11 Carrano C J & Bonadies J A, *J Am chem Soc*, 108 (1986) 4088.
12 Chakravarty J, Dutta S, Dey A & Chakravorty A, *J chem Soc, Dalton Trans*, (1994) 557.
13 Caira M R, Haigh J M & Nassimbeni L R, *J inorg nucl Chem*, 34 (1972) 3171.
14 Pessoa J C, Silva J A L, Vieira A L, Vilas-Boas L, Brien P O & Thornton P, *J chem Soc, Dalton Trans*, (1992) 1745.
15 Cornman C R, Kampf J, Lah M S & Pecoraro V L, *Inorg Chem*, 31 (1992) 2035.
16 Ballhausen C J & Gray H B, *Inorg Chem*, 1 (1962) 111.
17 Basu P, Pal S & Chakravorty A, *J chem Soc, Dalton Trans*, (1991) 3217.
18 Hausan G R, Kabanos T A, Keramidas A D, Mentzafos D & Terzis A, *Inorg Chem*, 31 (1992) 2587.