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Spectroscopic and Polarographic Studies of Novel Imidazole Adduct of Ammonium Trioxovanadate(V). A Solution and Solid State Study

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Complex formation between ammonium trioxovanadate(V) and imidazole has been studied and characterized by FT IR, UV/Vis, thermal analysis (TG, DTA, DTG) and polarographic techniques. Species formed in solid phase yield a yellow coloured product exhibiting an absorbance maximum at 400 nm. The FT IR spectra show that the inclusion of imidazole has a significant influence on the structure and the hydrogen bonding pattern in NH_4VO_3. Species formed in aqueous solution has been examined by voltammetry. Formation of an adduct of trioxovanadate(V) with imidazole onto dropping mercury electrode followed by reduction of the sample in DCP of the complex in 0.05 M NH_3/NH_4Cl buffer (pH 9.08) resulted in a single peak at –0.875 V.

Key words: ammonium trioxovanadate(V), FT IR, UV/Vis, thermal analysis, voltammetry, imidazole adduct

A variety of biological systems involving vanadium have emerged in the past years pointing on the significance of this metal in nature [1]. Prominent among those stand metalloproteins and metalloenzymes in biological active centers of which vanadium evolves as metal catalyst bound to amino acid residues and organic cofactors. Vanadium appears equally active outside of protein systems, either stimulating or inhibiting their biological function [2,3]. Interest in the chemistry of oxovanadium complexes has increased enormously in recent decades [4–9]. The increasing attention devoted to this type of compounds is mainly due to the functions of vanadium in several biological processes [10–11]. Basic research on the coordination chemistry of oxovanadium complexes has become essential for the knowledge of the behavior of these systems [12–14]. On the other hand, the imidazole ring has several unique features that count for its wide spreading utility in nature. It often occurs in the active centre of various metalloenzymes. Transition metal complexes with imidazole-containing ligands provide information on the mechanistic details of the enzymatic reactions. Model compounds mimicking the main features of active sites have long been used to characterize better the relation between structure and function of a large

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number of metalloproteins. Understanding the trace metabolism of vanadium is an exceedingly challenging problem, which not only requires a detailed knowledge concerning the biological systems, but also the complex vanadium chemistry. Recently, vanadium compounds with specific coordination number and stability have been characterized and developed [15]. Also, the process of how different biological systems respond to these compounds has been studied [10,16]. Vanadium(V) ion forms complexes with four-coordinate "ground state phosphate analogue" geometry, five-coordinate "transition state phosphate analogue" geometry or six-coordinate "metal ion" geometry [17]. Understanding vanadium's coordination preferences is crucial when embarking on compound design and for exploring potential mechanisms of action of vanadium in biological systems. Nevertheless, coordination properties of vanadium compounds are yet far from being well known. The complex chemistry of vanadium requires that both structures in the solid state and in solution must be examined. The present paper represents a summary of the spectral and electrochemical investigations of a novel imidazole adduct of ammonium trioxovanadate(V), to support biological studies of metabolic cycles and target compounds affected by vanadium compounds.

EXPERIMENTAL

Reagents and instruments: Imidazole and NH_4VO_3 were purchased from Merck and applied without further purification. In the voltammetric experiments, 0.05 M NH_3/NH_4Cl buffer (pH 9.08) prepared from analytical purity grade chemicals was used as supporting electrolyte. All solutions were prepared in deionized triply-distilled water just before use and protected from light and air.

Thermal analyses were performed on a Rigaku TG8110 thermal analyzer in static air atmosphere (Pt crucibles, sample mass about 9 mg, heating rate 10°C/min). The FT IR spectra were recorded with a Perkin–Elmer System 2000 FT IR interferometer from pressed KBr pellets, in a P/N 21525 temperature-controlled cell (Graseby Specac) with KBr windows. All together 16 background and 32 sample scans at resolution of 4 cm^{-1} were averaged for each spectrum. Electronic spectra in the 900–190 nm range were recorded on a Unicam V2–100 UV/Vis spectrophotometer (1 cm cell length). Polarographic experiments were performed with an EG&G PAR Model 384B polarographic analyzer connected to an EG&G PARC Model 303A polarographic stand (Princeton, NJ, USA). A dropping mercury electrode (DME) and an Ag|AgCl|saturated KCl reference electrode were used. The auxiliary electrode was a Pt wire. Voltammograms were recorded with a Houston Instrument DMP–40 plotter (Austin, TX, USA).

Preparation and spectroscopic measurements: ***FT IR spectra:*** Imidazole in stoichiometric amounts was added to ammonium trioxovanadate(V) solution. The reaction mixture was stirred at lowered temperature for complex formation. Then, absolute EtOH was added to the yellow solution to obtain a yellow precipitate, which was furthermore stirred for 10 min. The precipitate was filtered off, washed with small amounts of EtOH and dried *in vacuo*. It was recrystallized from absolute EtOH and used to record the FT IR spectrum.

UV/Vis spectra: Electronic spectra of the mixtures with ambient mole ratio of both vanadate(V) and imidazole in aqueous solutions were recorded. The changes in absorbance at the maximum absorption wavelength of these mixtures were monitored.

Polarographic measurements: The polarographic measurements were carried out in 0.05 M NH_3/NH_4Cl buffer (pH 9.08) as supporting electrolyte. Prior to each experiment, the electrolyte was purged with N_2 for 8 min. A known volume of the standard solution was added to the deaerated polarographic cell and the direct current polarogram recorded. The experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Thermal analysis: The composition of the imidazole adduct of ammonium trioxovanadate(V) was checked by thermal analysis (Table 1). Initial dehydration of the complex is followed by endothermic loss of imidazole, accompanied by complex appearance of the DTG curve, typical for removal of heterocyclic *N*-bases. Ammonia and water are then released in several overlapped exothermic steps, finally leading to V_2O_5, which melts at 674.8°C. The closest formula estimated from the thermal analysis is $(NH_4)(C_3N_2H_4)_{0.25}(VO_3)\cdot xH_2O$ ($x \approx 0.15$). It can be presumed, therefore, that one imidazole molecule is included for each four ammonium trioxovanadate(V) units; nevertheless, the present data are not sufficient to give the stoichiometry of the compound.

Table 1. Thermal (TG, DTG and DTA) data for the imidazole adduct of ammonium trioxovanadate(V).

Stage	Temp. range / °C	DTA peaks / °C[a]	Mass loss / %		Leaving species
			Calculated	Experimental	
1	81–139	97(–), 109(–)	1.98	2.00	H_2O
2	160–253	212(–)	12.45	13.93	imidazole
3	253–423	327(+), 343(+), 395(+)	19.05	21.69	NH_3, H_2O

[a] Symbols denote: (–) – endothermic, (+) – exothermic.

Spectral characterization of the imidazole adduct of ammonium trioxovanadate(V). ***FT IR spectra:*** The 4000–400 cm^{-1} region in the FT IR spectrum of the imidazole adduct of ammonium trioxovanadate(V) (AmImV) is presented in Fig. 1. The prominent, relatively broad band* with a maximum at 3435 cm^{-1} is assigned to stretchings of relatively weakly hydrogen-bonded XH groups (X = N or O). The presence of NH_4^+ ions and H_2O molecules is furthermore demonstrated by the appearance of bands from the ammonium HNH deformation mode, ν_4 [18], with centroid at 1426 cm^{-1} (probably overlapped with the imidazole mode expected around 1452 cm^{-1} [19]) and the water bending mode (ν_3) at 1630 cm^{-1}. The significant blue shift of the ammonium ν_4 band in the spectrum of AmImV from the analogous mode of NH_4VO_3 (1415 cm^{-1}) demonstrates that inclusion of imidazole (concurrent proton donor) significantly influences the hydrogen bonding pattern in NH_4VO_3. The external ammonium modes are weak bands overlapped with the imidazole bands below 480 cm^{-1}. The complex absorption extending from about 3320 cm^{-1} down to about 2100 cm^{-1} is characteristic for imidazole NH stretching mode, subject to Fermi-resonance with non-fundamental modes in the same region [19,20]. Medium strong to weak imidazole bands corresponding to the imidazole modes ν_5, ν_7, ν_8, ν_{10}, ν_{11}, ν_{12} and ν_{13}, and expected at 1567, 1452, 1319, 1186, 1143, 1098 and 1060 cm^{-1} from the inelastic neutron scatter-

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* It was confirmed by means of difference spectroscopy that this band is not due to presence of humidity.

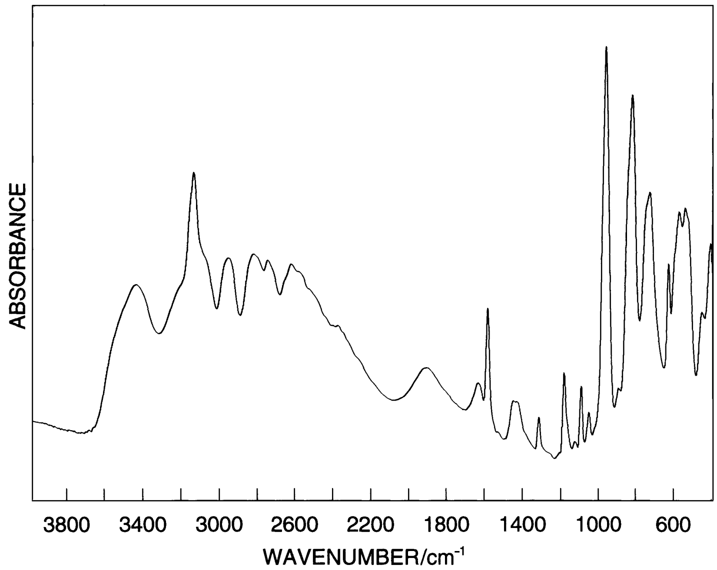

Figure 1. The 4000–400 cm^{-1} region in the FT IR spectrum of imidazole adduct of ammonium trioxovanadate(V).

ing studies [20] could be identified as the bands at 1583, 1448, 1314, 1185, 1126, 1094 and 1053 cm^{-1}, respectively, in the spectrum of AmImV. It was an early conclusion, that bands owing to the internal vibrations of heterocylic bases are not subject to drastic spectral changes other than some minor shifts and splittings [21]. The broad feature at 1910 cm^{-1} corresponds to a non-fundamental mode, also present in the spectrum of solid imidazole [20]. Close reproduction of imidazole modes in the spectrum of AmImV indicates that the molecular structure of imidazole is not changed appreciably upon inclusion in NH_4VO_3. The VO stretching mode is observed as a strong sharp band at 965 cm^{-1} (Fig. 1) in the spectrum of AmImV. Compared to NH_4VO_3 (911 and 895 cm^{-1}) the band is blue-shifted, implying remarkable perturbations in the coordination sphere of the V(V) ions.

Electronic spectra: The electronic spectra of imidazole (Im) in water consist of a strong band at 256 nm ($\pi \rightarrow \pi^*$) (Fig. 2). A solution of AmImV in water gave a spectrum very similar to that of Im; however, a weak broad band at 400 nm was also detected. This peak can be assigned as metal-to-ligand charge-transfer transition ($\mathrm{Im}\pi^* \rightarrow \mathrm{Vd}\pi$) [22]. Similarly, the complex of vanadium(V) with N-p-bromophenylthiobenzohydroxamic acid showed a maximum absorbance at 405 nm [23]. The highest energy band at 200–240 nm can be attributed to an $n \rightarrow \pi^*$ type charge transfer between the solvent and the metal complex [24]. Complexation of the Im nitrogen reduces the π-electron density on the nitrogen itself and enhances its acceptor properties [25].

Voltammetric measurements: ***Direct current polarography (DCP) of imidazole adduct of ammonium trioxovanadate(V):*** For final clarification of the inclusion of imidazole into ammonium trioxovanadate(V), it appeared necessary to carry out

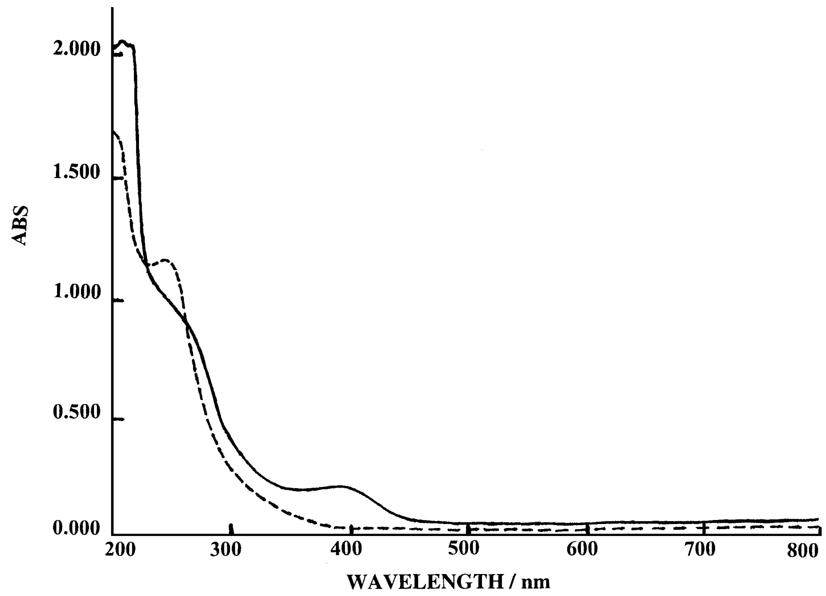

Figure 2. The electronic spectra of imidazole (---------) and the imidazole adduct of ammonium trioxovanadate(V)(———).

voltammetric measurements. A DCP polarogram of ammonium trioxovanadate(V) solution in absence of imidazole produces a reduction wave ($E_{1/2} = -1.065$ V) in 0.05 M NH_3/NH_4Cl buffer (pH 9.08) (Fig. 3). This wave is inferred from reduction of V(V)

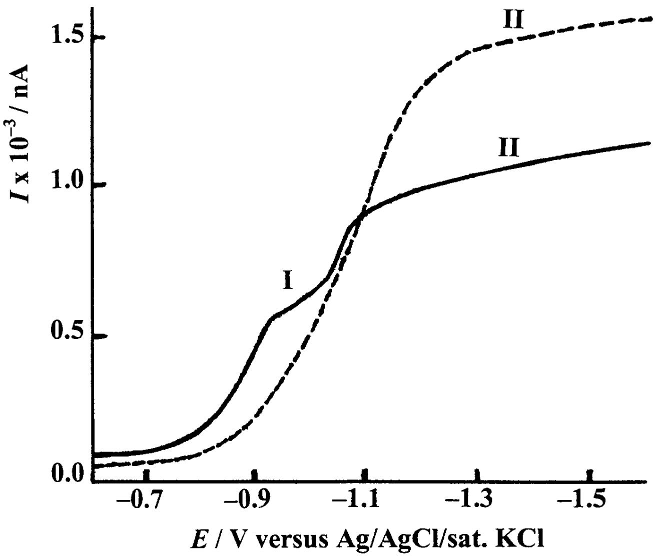

Figure 3. DCP polarograms of 1.96×10^{-4} M NH_4VO_3 solution in the absence of imidazole (– – – –) and in the presence of 1.32×10^{-3} M imidazole (——) at 0.05 M NH_3/NH_4Cl buffer (pH 9.08). **I**, the reduction wave for imidazole adduct of ammonium trioxovanadate(V); **II**, the reduction wave for free ammonium trioxovanadate(V). Experimental conditions: drop time, 1 s; scan rate, 400 mVs^{-1}; drop size, medium.

to V(IV) [26]. Although it is well known that derivative compounds of Im are strongly adsorbed on the mercury electrode [27]; the DCP polarogram of Im in the absence of V(V) gave no wave. At pH 9.08 and with increasing Im concentration in the presence of ammonium trioxovanadium(V), a new wave ($E_{1/2} = -0.875$ V) appears at more positive potential than that of ammonium trioxovanadium(V), while the diffusion current of free ammonium trioxovanadium(V) decreases (Fig. 3). The wave ($E_{1/2} = -0.875$ V) can be attributed to AmImV. Literature survey reveals that the complexes of V(V) are often characterized by the means of adsorptive stripping voltammetry (*e.g.*, see [28]), using their adsorption properties on the mercury electrode (*e.g.*, adsorbed V(V)-pyrocatechol violet complex on Hg gives a peak at –0.8 V in urotropin buffer). Nevertheless, the technique is not appropriate to monitor complex formation studies.

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REFERENCES

1. Rheder T., *BioMetals*, **5**, 3 (1992).
2. Mendz G.L., Hyslop S.J. and Kuchel P.W., *Arch. Biochem. Biophys.*, **276**, 160 (1990).
3. Gresser M.J. and Tracey A.S., in "Vanadium in Biological Systems" Chasteen N.D. Ed., Kluwer, Dordrecht, 1990; pp. 63–79.
4. Braga D. and Sabatino P., *Acta Cryst.*, **C46**, 2308 (1990).
5. Neves A., Hörner M., Fenner H. and Strähle J., *Acta Cryst.*, **C49**, 1737 (1993).
6. Higes-Rolando F.J., Perez-Florindo A., Valenzuala-Calahorro C. and Martin-Ramos J.D., *Acta Cryst.*, **C50**, 1049 (1994).
7. Elvingson K., Crans D.C. and Pettersson L., *J. Am. Chem. Soc.*, **119**, 7005 (1997).
8. Rehder D., *Coordination Chem. Rev.*, **182**, 297 (1999).
9. Smith T.S., Root C.A., Kampf J.W., Rasmussen P.G. and Pecoraro V.L., *J. Am. Chem. Soc.*, **122**, 767 (2000).
10. Siegel H. and Siegel A. Eds., "Metal Ions in Biological Systems", vol. 31, Marcel Dekker, NY 1995.
11. Crans D.C., *Comments Inorg. Chem.*, **16**, 35 (1994).
12. Jiang F., Anderson O.P., Miller S.M., Chen J., Mahroof-Tahir M. and Crans D.C., *Inorg. Chem.*, **37**, 5439 (1998).
13. Hanson G.R., Sun Y. and Orvig C., *Inorg. Chem.*, **35**, 6507 (1996).
14. Keramidas A.D., Miller S.M., Anderson O.P. and Crans D.C., *J. Am. Chem. Soc.*, **119**, 8901 (1997).
15. Kempf J.Y., Maigret B. and Crans D.C., *Inorg. Chem.*, **35**, 6485 (1996).
16. Crans D.C., Felty R.A., Chen H., Eckert H. and Das N., *Inorg. Chem.*, **33**, 2427 (1994).
17. Ray J.W., Crans D.C., Zheng J., Burgner J.W., Deng H. and Mahroof–Tahir M., *J. Am. Chem. Soc.*, **117**, 6015 (1995).
18. Kearley G.J. and Oxton I.A., *Adv. Infrared Raman Spectrosc.*, **23**, 15 (1991).
19. Loeffen P.W. and Pettifer R.F., *J. Chem. Phys.*, **103**, 8444 (1995).
20. Majoube M., *J. Mol. Struct.*, **61**, 129 (1980).
21. Goldstein M., Monney F.E., Anderson A. and Gebbie A.H., *Spectrochim. Acta*, **21**, 105 (1965).
22. Çakır S., Biçer E. and Eleman A., *Transit. Met. Chem.*, in press.
23. Kumar A., Mathur N., Mathur P. and Mathur S.P., *Rev. Roum. Chim.*, **43**, 3 (1998).
24. Foster R., "Organic Charge Transfer Complexes", Academic Press, London, 1969.
25. Ramadan R.M., Attia A.S. and El-Shahat M.F., *Polyhedron*, **15**, 301 (1996).
26. Heyrovský J. and Kůta J., "Principles of Polarography", Academic Press, NY 1966, p. 546.
27. Slojkowska R. and Jurkiewicz-Herbich M., *Polish J. Chem.*, **73**, 541 (1999).
28. Agra-Gutierroz C. and Compton R.G., *Electroanalysis*, **10**, 204 (1998).