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Template Synthesis of Oxovanadium(IV) Complexes with Tetradentate 16-Membered N_6 Macrocyclic Ligands

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The macrocyclic complexes [VO(mac)] (where mac = 16-membered macrocyclic ligands derived by condensation of 2,6-diaminopyridine with β-diketones) have been synthesised by *in situ* method using oxovanadium(IV) cation as template. The complexes have been characterized on the basis of elemental analyses, electrical conductance, magnetic susceptibility measurements and spectral (infrared and electronic) data. The macrocyclic ligands act as tetradentate dianions and oxovanadium(IV) complexes are five co-ordinated. Pyridine nitrogens remain uncoordinated.

INTRODUCTION

Though a lot of work has appeared on transition metal complexes with planar tetraaza macrocyclic ligands due to their possible use as substitute for porphyrins and metalloporphyrins[1–4], relatively little has been presented on their vanadium complexes[5]. After recognition of essential role of vandium in both plants and animals[6–11] with numerous physiological effects[12–16], several studies have been performed and oxovanadium(IV) ion has been found to show inhibitory effect on Na^+, K^+-ATPase[17] and alkaline phosphatase[18]. Thus, keeping in view the biochemical importance of vanadium, a new series of oxovanadium(IV) complexes with 16-membered macrocyclic ligands derived by condensation of 2,6-diaminopyridine with β-diketones *viz.*, acetylacetone, benzoylacetone, thenoyltrifluoroacetone and dibenzoylmethane have been synthesised and characterized.

EXPERIMENTAL

All the solvents and chemicals used were reagent grade B.D.H. products. The β-diketones and 2,6-diaminobenzene obtained from SRL and Aldrich respectively, were used without further purification.

In situ Preparation of Oxovandium(IV) Complexes with Macrocyclic Ligands Derived by Condensation of 2,6-Diaminopyridine and β-Diketones, [VO(mac)]

A general procedure was adopted as follows:

A solution of 2,6-diaminopyridine (0.02 mol) in 20 ml ethanol was mixed with an appropriate β-diketone (0.02 mole) in 20 ml ethanol and the mixture was

refluxed for 1 hr. To this mixture, vanadyl sulphate (0.01 mol) solution in 20 ml methanol was added followed by addition of glacial acetic acid just to make the reaction mixture slightly acidic and a green color precipitate was obtained. The reaction mixture was further refluxed for 5–6 hrs when colour of the solution intensified. The solvent was removed under *vacuo* and solid products were obtained. The green complexes were thoroughly washed with methanol and then ethanol and dried in vacuo (yield 39–44%). The decomposition temperature, yield and analytical data of the complexes are given in Table 1.

TABLE 1
PHYSICAL AND ANALYTICAL DATA OF VO^{2+} COMPLEXES

Complex	Decomp. temp (°C)	Calc. (Found) %				μ_{eff} BM (300°K)
		C	H	N	V	
$[VO(mac^1)]$ $C_{20}H_{20}N_6OV$	288	58.4 (58.3)	4.9 (4.8)	20.4 (20.3)	12.4 (12.3)	1.75
$[VO(mac^2)]$ $C_{30}H_{24}N_6OV$	290	67.3 (67.2)	4.5 (4.4)	15.7 (15.7)	9.5 (9.5)	1.73
$[VO(mac^3)]$ $C_{26}H_{14}N_6S_2F_6V$	278	47.6 (47.5)	2.1 (2.0)	12.8 (12.6)	7.8 (7.7)	1.74
$[VO(mac^4)]$ $C_{40}H_{28}N_6OV$	286	72.8 (72.7)	4.2 (4.1)	12.7 (12.6)	7.7 (7.6)	1.76

where (mac^1) = Macrocyclic ligand derived by condensation of 2,6-diaminopyridine with acetylacetone
(mac^2) = Macrocyclic ligand derived by condensation of 2,6-diaminopyridine with benzoylacetone
(mac^3) = Macrocyclic ligand derived by condensation of 2,6-diaminopyridine with thenoyltrifluoroacetone
(mac^4) = Macrocyclic ligand derived by condensation of 2,6-diaminopyridine with dibenzoylmethane

RESULTS AND DISCUSSION

The macrocyclic complexes of oxovanadium(IV) were synthesized using *in situ* method by refluxing the reaction mixture of vanadyl sulphate, 2,6-diaminopyridine, β-diketone in 1 : 2 : 2 molar ratio in aqueous ethanol in slightly acidic medium. The reactions appear to proceed according to the following equation:

$$VOSO_4 \cdot H_2O + \text{2,6-diaminopyridine} + \beta\text{-diketone}$$

Glacial acetic acid | ethanol

$$\downarrow$$

$$[VO(mac)] + 5H_2O + H_2SO_4$$

where mac = 16-membered macrocyclic ligands derived by condensation of 2,6-diaminopyridine with different β-diketones.

The elemental analyses (Table 1) of complexes show 1 : 1 metal to ligand stoichiometry. The measurement of molar conductivity of the oxovanadium(IV) complexes in dimethylformamide showed non-electrolytic nature.

The important spectral (infrared and electronic) bands for the complexes are listed in Table 2. The macrocyclic complexes of oxovandium(IV) show various unaltered pyridine ring vibrations at *ca.* 1590 cm^{-1} (8a), 600 cm^{-1} (6a) and 410 cm^{-1} (16b) indicating the non-coordination of pyridine nitrogen to metal ion[19,20]. The complexes show strong vibrations at about 1615–1620 cm^{-1} which normally appear at higher wavenumbers (20–25 cm^{-1}) in free ligands[21]. The lowering of this band indicates co-ordination of azomethine nitrogens to the vandium[21-23]. This is further supported by appearance of a band at around 310 cm^{-1} which may be assigned to ν(V–N) vibration[24]. The bands due to free amino or keto group are not observed in the spectra of complexes which lead to a conclusion that the two molecules of β-diketones have condensed with two molecules of 2,6-diaminopyridine. A large number of bands also arise due to the phenyl ring and different alkyl groups, but definite assignments of these bands are not possible due to the complexity of the spectrum arising out of the overlap of these absorptions. The oxovanadium(IV) complexes show a strong band at around 980 cm^{-1} which is assigned to ν(V = 0) vibration[5].

The magnetic moment values of the oxovanadium(IV) complexes lie in the range 1.73–1.76 BM at room temperature. The complexes exhibit three bands in the regions 11260–11890 cm^{-1}, 15170–15910 cm^{-1} and 21340–22180 cm^{-1} (Table 2). These spectra resemble those of other five-coordinate oxovanadium(IV)

TABLE 2
SOME CHARACTERISTIC INFRARED AND ELECTRONIC SPECTRAL BANDS OF THE COMPLEXES

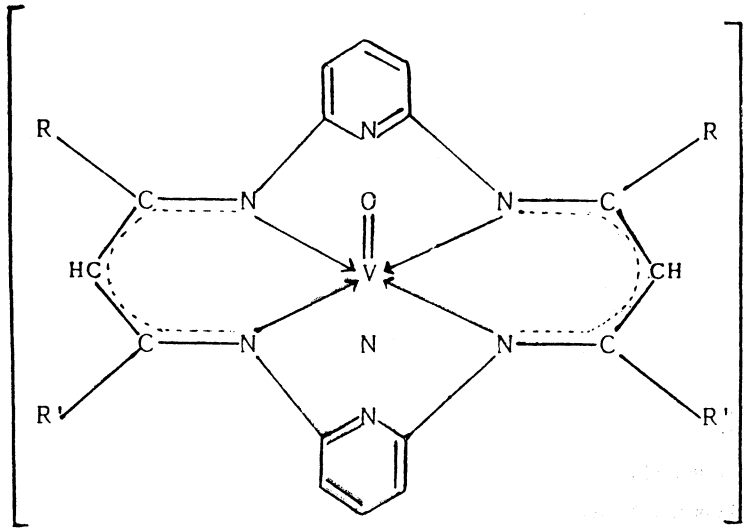
Complex	Infrared spectra (cm^{-1})			Electronic spectra (cm^{-1})		
	ν (>C=N)	ν (V–N)	ν (V=O)	$^2B_2 \rightarrow {}^2E$	$^2B_2 \rightarrow {}^2B_1$	$^2B_2 \rightarrow {}^2A_1$
[VO(mac^1)]	1620s	310m	980s	11,460	11,510	21,610
[VO(mac^2)]	1620s	310m	980s	11,630	15,750	21,820
[VO(mac^3)]	1615s	310w	970m	11,260	15,170	21,340
[VO(mac^4)]	1620s	310s	980s	11,890	15,910	22,180

s = strong; m = medium; w = weak

complexes[25-28]. Wasson *et al*[29]. have reported an energy level scheme: $d_{xy} < d_{yz} < d_{xz} < d_{x^2-y^2} < d_{z^2}$ interpret the electronic spectra of distorted five-coordinate square pyramidal oxovanadium(IV) complexes. This scheme is similar to that proposed by Ballhausen and Grey[30], except for the splitting of d_{xz} and d_{yz} levels.

Accordingly, the bands observed for the oxovanadium(IV) complexes can be assigned to $^2B_2 \rightarrow {}^2E$, $^2B_2 \rightarrow {}^2B_1$ and $^2B_2 \rightarrow {}^2A_1$ transitions respectively. One more band observed in the region 35570–36000 cm^{-1} may be assigned[31] to transitions of the azomethine linkage (>C=N).

On the basis of above studies, the following tentative structure may be proposed for macrocyclic complexes of oxovanadium(IV).



where

R	R′	β-Diketones
CH_3	CH_3	Acetylacetone
C_6H_5	C_6H_5	Benzoylacetone
C_4H_3S	CF_3	Thenoylitrifluoroacetone
C_6H_5	C_6H_5	Dibenzoylmethane

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REFERENCES

1. G.A. Melson, Coordination Chemistry of Macrocyclic Compounds, Plenum, New York (1979).
2. W. Radecka-Paryzek, *Inorg. Chim. Acta*, **45**, L 147 (1980).

3. K.K. Abid, D.E. Fenton, U. Casellato, P.A. Vigato and R. Graziani, *J. Chem. Soc., Dalton Trans.*, 351 (1984).
4. S. Balasubramanian, D. Abdul Gani and M. Kandaswami, *Synth. React. Inorg. Met.-Org. Chem.*, **18**, 285 (1988).
5. H.D.S. Yadav, S.K. Sengupta and S.C. Tripathi, *Inorg. Chim. Acta*, **128**, 1 (1987).
6. G. Wilkinson ed., "Comprehensive Coordination Chemistry", Pergamon Press, Vol. 6, p. 665 (1987).
7. E.J. Underwood, "Trace Elements in Human and Animal Nutrition", Academic Press, London, p. 416 (1971).
8. K. Kustin and I.G. Macara, *Comments Inorg. Chem.*, **2**, 1 (1982).
9. N.D. Chasteen, *Struct. & Bonding*, **53**, 105 (1983).
10. E.J. Baran, Quimica Bio-inorganica. Ediciones Faba, La Plata, Argentina (1984).
11. R.L. Robson, R.R. Eady, T.H. Richardson, R.W. Miller, M. Hawkins and J.R. Postgate, *Nature*, **322**, 288 (1986).
12. B.J. Bowman and C.W. Slayman, *J. Biol. Chem.*, **254**, 2928 (1979).
13. G.R. Willsky, *J. Biol. Chem.*, **254**, 3326 (1979).
14. F. Yoshimura and A.F. Brodie, *J. Biol. Chem.*, **256**, 12239 (1981).
15. J.P.F.C. Roosi, P.J. Garrahan and A.F. Rega, *Biochem. Biophys. Acta*, **648**, 145 (1981).
16. A. Butler, S.M. Parsons, S.K. Yamagata and R.I. De La Rosa, *Inorg. Chim. Acta*, **163** 1 (1989)
17. P. North and R.L. Post, *J. Biol. Chem.*, **259**, 4971 (1984).
18. V. Lopez, T. Stevens and R.N. Lindquist, *Arch. Biochem. Biophys.*, **175**, 31 (1976).
19. A.B.P. Lever, D.A. Baldwin and R.V. Parish, *Inorg. Chem.*, **8**, 107 (1969).
20. W.R. McWhinne, *Coord. Chem. Rev.*, **5**, 293 (1970).
21. V.B. Rana, P. Singh, D.P. Singh and M.P. Teotia, *Transition Met. Chem.*, **7**, 174 (1982).
22. S. Chandra and K.K. Sharma, *Transition Met. Chem.*, **8**, 1 (1988).
23. W.U. Malik, R. Bembi and R. Singh, *Inorg. Chim. Acta*, **68**, 223 (1983).
24. J.R. Ferraro, "Low Frequency Vibrations of Inorganic and Coordination Compounds", Plenum, New York (1971).
25. D.N. Sathyanarayana and C.C. Patel, *Indian J. Chem.*, **3**, 486 (1965).
26. L. Sacconi and U. Campigli, *Inorg. Chem.*, **5**, 606 (1966).
27. S. Yamada and Y. Kuge, *Bull. Chem. Soc. Jpn.*, **42**, 152 (1969).
28. A.K. Srivastava, R.K. Agarwal, M. Srivastava, V. Kapur, S. Sharma and P.C. Jain, *Transition Met. Chem.*, **7**, 41 (1982).
29. H.J. Stocklosa, J.R. Wasson and M.J. McCormick, *Inorg. Chem.*, **13**, 592 (1964).
30. C.J. Ballhausen and H.B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
31. P.C.H. Mitchell and J.A. Valero, *Inorg. Chim. Acta*, **71**, 179 (1983).

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