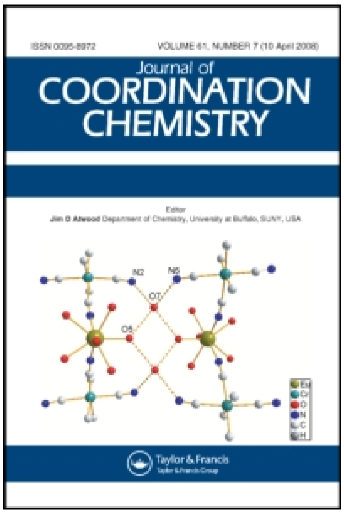

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OXOVANADIUM(IV) COMPLEXES WITH JÄGER-TYPE LIGANDS

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Oxovanadium(IV) complexes, [VO(J-R)], where H_2J-R is a Jäger-type ligand with bridging group R (ethylene *o*-phenylene or 4-methyl-*o*-phenylene), have been synthesized. Condensations of the complexes with diamines give products but as sticky, insoluble materials. An alternative method has been used to obtain cyclic oxovanadium(IV) complexes.

KEYWORDS: Oxovanadium(IV), Jäger Ligands, macrocycles, synthesis.

INTRODUCTION

In recent years, a few papers have appeared on transition metal complexes involving Jäger-type ligands.[1–4] The interest in such compounds is due to their potential as starting materials for synthetic protein models,[4] their redox properties[5,6] and their behaviour as low dimensional materials.[7] One characteristic of Jäger complexes is the ability to form a macrocyclic ring when reacted with diamines.[8,9] The cyclization is facilitated by the electron withdrawing ability of the acetyl group attached to the γ-position of the ligand. This paper reports the synthesis and properties of oxovanadium(IV) complexes with Jäger ligands derived from the condensation of 3-(ethoxymethylene)-2,4-pentanediene with ethylenediamine, *o*-phenylenediamine or 4-methyl-*o*-phenylenediamine.

RESULTS AND DISCUSSION

Acyclic Complexes

Reactions of oxovanadium(IV) sulphate with Jäger ligands (H_2J-R) in ethanol yielded complexes of the type VO(J-R). The procedure used for the preparation and isolation of these compounds gave materials of good purity as supported by analyses (Table I). The complexes are green or brown, and soluble in DMF, DMSO, benzene and nitrobenzene. Electrical conductance measurements in DMF show that they are essentially non-electrolytes.

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Table I Reactions of oxovanadium(IV) complexes with Jäger type ligands

Reactants	Mol ratio	Reflux time (hours)	Product*	Colour	Yield (%)	Decomp. temp. (°C)
$VOSO_4 \cdot 5H_2O$ + H_2J-en	1:1	5	[VO(J-en)]	Olive	62	210
$VOSO_4 \cdot 5H_2O$ + H_2 J-ph	1:1	5	[VO(J-ph)]	Brownish yellow	68	>250
$VOSO_4 \cdot 5H_2O$ + H_2J-mph	1:1	6	[VO(J-mph)]	Dark brown	55	>250
$VOSO_4 \cdot 5H_2O$ + mac_1	1:1	15	[VO(mac_1)]	Brown	22	200
$VOSO_4 \cdot 5H_2O$ + mac_2	1:1	15	[VO(mac_2)]	Brown	25	230

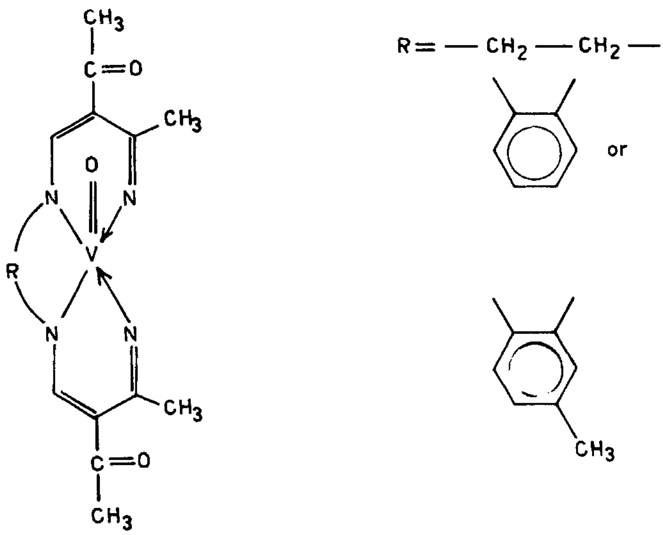
*H_2J-en = Jäger ligand derived from 3-(ethoxymethylene)-2,4-pentanedione and ethylene diamine; H_2J-ph = Jäger ligand derived from 3-(ethoxymethylene)-2,4-pentanedione and *o*-phenylenediamine; H_2J-mph = Jäger ligand derived from 3-(ethoxymethylene)-2,4-pentanedione and 4-methyl-*o*-phenylenedianine; mac_1 = Cyclic ligand derived from H_2J-en and ethylenediamine; mac_2 = Cyclic ligand derived from H_2J-ph and *o*-phenylenediamine.

Room tempeature magnetic moments of the oxovanadium(IV) complexes lie in the range 1.70–1.78 B.M. These values are within the range reported for other oxovanadium(IV) complexes, where the orbital contribution is completely quenched due to low symmetry. Electronic spectra of the complexes in DMF show bands in the regions 10900–12300, 15100–15800 and 21000 – 22500 cm^{-1}. These are at the same positions as reported for other five-coordinate oxovanadium(IV) complexes. Several schemes have been advanced to interpret the electronic spectra of oxovanadium(IV) complexes.[10] The scheme developed by Ballhausen and Gray[11] can account well for complexes of both idealized and low symmetry. The bands may be assigned to $b_2 \rightarrow e_\pi^*$ ($^2B_2 \rightarrow E$), $b_1 \rightarrow b_1^*$ ($^2B_2 \rightarrow {}^2B_1$) and $b_2 \rightarrow a_1^*$ ($^2B_2 \rightarrow {}^2A^1$) transitions in increasing order of energy.

Infrared spectra of the ligands show a band at 3150 cm^{-1} due to ν(NH) which disappears in the corresponding complexes, thus suggesting coordination through the amine nitrogen after deprotonation. The ν(V-N) band appears at *ca* 430–420 cm^{-1}. Ligands show one strong band at *ca* 1680-cm^{-1} due to ν(C = O). The spectra of complexes show the C = O band shifted to lower frequency with respect to the free ligand, but with a noticeable shoulder remaining at the same wavelength where the strong C = O band appears for the free ligand. This may be due to the fact that only two of the four C = O groups can be involved in coordination. This is further supported by the appearance of medium bands at *ca* 490–475 cm^{-1} in the complexes, assignable to ν(V – O). In addition, the IR spectra of all complexes show bands at *ca* 970 cm^{-1} which may be assigned[10] to ν(V = O) vibrations. Thus, on the basis of available data, structure (**I**) may be proposed for the complexes [VO(J-R)].

Cyclic Complexes

Reactions of complexes (**I**) with diamines (ethylene-diamine, *o*-phenylenediamine, 4-methyl-*o*-phenylene diamine) have been studied in refluxing anhydrous solvents in order to obtain macrocyclic products. Several attempts were made to cyclize the complexes but unfortunately these always resulted in decomposition of the complexes and formation of sticky, insoluble materials. Therefore, an alternative method has been developed to obtain the cyclic complexes. This method involves the following steps, as given in Scheme 1.



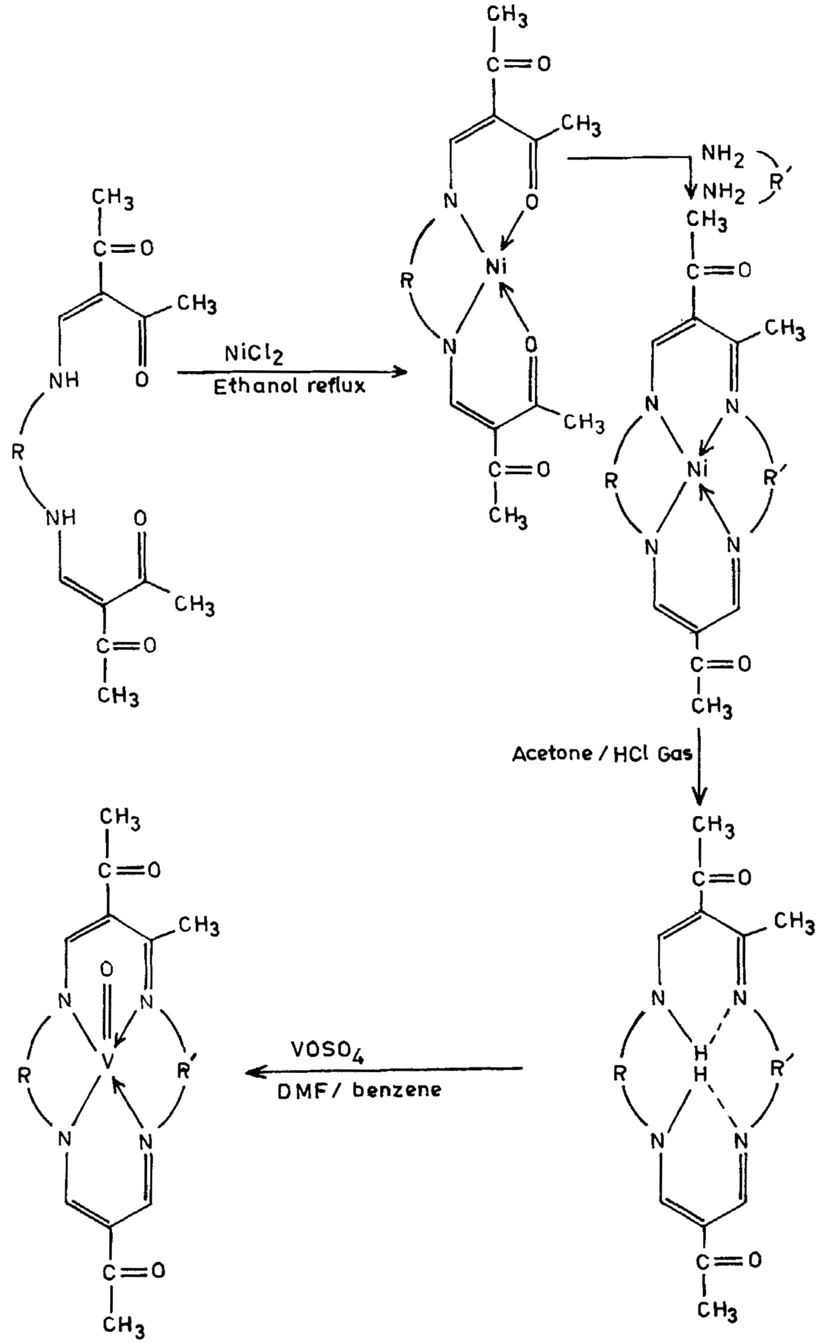
(I)

Figure 1

1. Reaction of nickel(II) chloride with Jäger-type ligands and isolation of complexes of type [Ni(J-R).[2]
2. Reaction of complexes [Ni(J-R)] with diamines and isolation of cyclic products [Ni(mac)].
3. Isolation of free cyclic ligands by passing HCl gas through an acetone solution of [Ni(mac).[2]
4. Reactions of cyclic ligands with oxovanadium(IV) sulphate and isolation of complexes [Vo(mac)] in small yield.

The cyclic complexes are dark coloured solids which are soluble only in DMF and DMSO. Electrical conductance measurements in DMF indicate their non-electrolytic nature. Magnetic moments of the cyclic oxovanadium(IV) complexes lie in the range 1.71–1.74 B.M.

Electronic and infrared spectra of the cyclic products are quite similar to those of the acyclic precursors. The electronic spectra of the cyclic products show three similar bands. However, the IR spectra do not show any band near 1640 cm^{-1} (due to coordianted C = 0). Instead, these complexes show one band near 1610 cm^{-1} which is attributed to a C = N stretch of the newly formed azomethine linkage (in cyclic ligands, this band appeas at *ca* 1625 cm^{-1}). The ν (V = O) band appears near 975 cm^{-1}. These observations clearly indicate[4] that two C = O groups in the acyclic complexes condense with amino groups of the appropriate diamine. Structure studies using single-crystal methods are proceeding.


NiCl2
Ethanol reflux
NH2
NH2
R'
Acetone / HCl Gas
VOSO4
DMF / benzene
R
Ni
V
CH3
C=O
N
NH
O

Scheme 1

EXPERIMENTAL

Oxovanadium(IV) sulphate was obtained from Aldrich and was estimated gravimetrically as oxide. Estimation of carbon and hydrogen was done by CDRI, Lucknow and nitrogen by the Kjeld'ahl method. The ligands were prepared as reported earlier.[4] Details of physical measurements have been described earlier.[10]

Preparation of acyclic oxovanadium(IV) complexes

Oxovanadium(IV) sulphate (0.02 mol) dissolved in methanol (25 cm^3) was added to a refluxing solution of the appropriate Jäger-type ligand (0.02 mol) dissolved in methanol (20 cm^3). The reaction mixture was refluxed for 5-6 hours when a coloured precipitate was obtained. The precipitate was washed with methanol and dried. Yield 55–68%.

Preparation of cyclic oxovanadium(IV) complexes

Cyclic complexes of oxovanadium(IV) were prepared starting with nickel complexes of Jäger-type ligands. Nickel(II) complexes were prepared according to the method given in the literature.[2] The preparation of cyclic oxovanadium(IV) complexes involves the following.

A stream of anhydrous hydrogen chloride was passed through a magnetically stirred suspension of nickel(II) complex (0.05 mol) in 150 cm^3 of acetone. The colour of the reaction mixture changed slowly from dark green to orange yellow and a yellow precipitate began to appear. After about 15 minutes, the passage of hydrogen chloride was stopped and the tightly closed reaction flask was left to stir overnight. Crystalline solid material which had accumulated was filtered off, washed with acetone and dried. It was then treated with dilute (1:10) hydrochloric acid to dissolve any nickel chloride. Yellow, undissolved solid was filtered off, washed carefully with dilute hydrochloric acid and then immediately with acetone and dried. Yield ~48%.

Vanadyl sulphate (0.02 mol) dissolved in methanol (15 cm^3) was poured into a refluxing solution of appropriate cyclic ligand (0.02 mol) in a mixture (30 cm^3) of dimethylformamide and benzene (1:1). The reaction mixture was refluxed for about 15 hours when the colour of the solution turned brown. Solvent was removed under vacuum at room temperature and the brown solid obtained was thoroughly washed with methanol, hot benzene and dried under vacuum. Yield 22–26%.

For the sake of brevity, the details of the reactions are summarized in Table I. Analytical data for the complexes are given in Table II.

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Table II Analytical data for oxovanadium(IV) complexes with Jäger type ligand

Complex*	Found(%)				Calcd.(%)			
	C	H	N	V	C	H	N	V
[VO(H_2-Jen)]	48.6	5.0	8.0	14.6	48.7	5.2	8.1	14.8
[VO(H_2-Jph)]	54.8	4.4	7.1	12.7	55.0	4.6	7.1	13.0
[VO(H_2J-mph)]	55.8	4.8	6.7	12.3	56.0	4.9	6.9	12.5
[VO(mac_1)]	50.2	6.1	15.5	14.2	50.4	6.2	15.7	14.3
[VO(mac_2)]	61.8	4.5	12.1	10.8	61.9	4.7	12.0	10.9

*H_2J-en = Jäger ligand derived from 3-(ethoxymethylene)-2,4-pentanedione and ethylene diamine; H_2J-ph = Jäger ligand derived from 3-(ethoxymethylene)-2,4-pentanedione and *o*-phenylenediamine; H_2J-mph = Jäger ligand derived from 3-(ethoxymethylene)-2,4-pentanedione and 4-methyl-*o*-phenylenedianine; mac_1 = Cyclic ligand derived from H_2J-en and ethylenediamine; mac_2 = Cyclic ligand derived from H_2J-ph and *o*-phenylenediaminc.

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