

Synthesis & Structural Studies of Oxovanadium(IV), Manganese(II), Iron(II), Cobalt(II), Nickel(II) & Copper(II) Complexes with a New Tetradentate Schiff Base Having O:N:N:O Donor System

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Received 22 July 1985; revised and accepted 23 September 1985

The complexes of a new quadridentate schiff base derived from 4-methyl-7-hydroxy-8-acetylcoumarin and ethylenediamine (AMUEN) with oxovanadium(IV), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been synthesised and characterised on the basis of their elemental analyses, conductivity, magnetic moment, TG and DT analyses, and infrared, electronic and ESR spectral data. Metal to ligand ratio in all the chelates has been found to be 1:1. The schiff base behaves in a diabasic tetradentate manner with O:N:N:O donor sequence. Oxovanadium(IV), Mn(II), Fe(II), Co(II) and Cu(II) complexes have been assigned octahedral stereochemistry and Ni(II) complex has been assigned a square planar geometry.

Coumarin (2H-1-benzopyran-2-one) and its derivatives have been found to exhibit antibiotic, antifungal, anticoagulating and plant growth regulating¹⁻⁴ activities and are also extensively used as analytical reagents⁵⁻⁷. Coumarin derivatives containing hydroxy, acetyl and phenylazo substituents have been employed as complexing agents⁸⁻¹⁰. Literature survey reveals that very little work has, however, been reported on schiff bases of coumarins^{11,12}. In recent years considerable interest has been shown in the synthesis of quadridentate schiff bases and their metal chelates. These may be regarded as models of biological interest¹³⁻¹⁶. Keeping this in view we report here the synthesis and characterisation of a new quadridentate schiff base derived from 4-methyl-7-hydroxy-8-acetylcoumarin and ethylenediamine (AMUEN) and its complexes with oxovanadium(IV), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

4-Methyl-7-hydroxy-8-acetylcoumarin was prepared by the reported procedure^{17,18}. All the other chemicals used were of AR grade.

The ligand AMUEN was prepared by refluxing two moles of 4-methyl-7-hydroxy-8-acetylcoumarin with one mole of ethylenediamine in ethanol for about one hour at pH 6-7. The yellow product so obtained was recrystallised from ethanol, m.p. 185°C.

The metal complexes were prepared by refluxing hot ethanolic solutions of metal chloride (0.01 mol) [except in the case of Fe(II) and oxovanadium(IV) complexes where aqueous ethanolic solutions were used] and the ligand (0.01 mol) for 2-3 hr on a water bath. The complexes separated on adjusting the pH to 7-8. The complexes thus separated were filtered, washed with ethanol/aqueous ethanol followed by pet. ether (60-80°) and dried *in vacuo*.

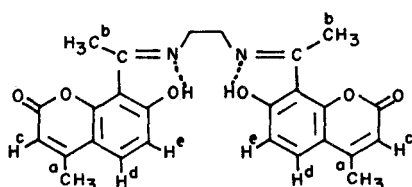
The IR spectra of the ligand and metal chelates were recorded in KBr in the range 4000-400 cm⁻¹ on a Shimadzu-435 IR spectrophotometer. The NMR spectrum of the ligand was recorded on an EM-390 NMR spectrometer. Elemental analyses were carried out by micro-analytical techniques. Metal estimations were done on a Perkin-Elmer 1280 atomic absorption spectrophotometer. Conductivity measurements were carried out using a digital conductivity meter 304 (Systronics). The electronic spectra of metal chelates were recorded on a DMR-21 UV-Vis spectrophotometer in the range 1300-300 nm in nujol at room temperature. The ESR spectra of Cu(II) and oxovanadium(IV) complexes were recorded on a Varian EPR-E₄ spectrometer as powder at room temperature. Thermogravimetric analysis was carried out on a manually operated thermobalance with a heating rate of 5°/min. Differential thermal analysis was carried out on Leed and Northrup DTA unit (USA) with a heating rate of 10°/min and sensitivity 100μv/inch. Magnetic susceptibilities of the complexes were measured at room temperature on a Faraday balance using Hg[Co(SCN)₄] as the calibrant.

All the complexes are coloured, stable towards air and moisture, decompose at high temperatures and are insoluble in common organic solvents.

The analytical data (Table I) of the complexes indicate the metal to ligand ratio as 1:1. Molar conductance values of the complexes in DMF at 30°C are in the range 20-30 mhos cm² mol⁻¹ suggesting their non-ionic character. The molecular weights determined cryoscopically in freezing DMF show them to be monomeric in nature.

The ¹H NMR spectrum of the ligand, AMUEN (structure I) was recorded in CDCl₃ and it was interpreted¹⁹ as follows: δ 2.38 (s, 6H, a-CH₃), 2.85 (s, 6H, b-CH₃), 5.95 (s, 4H, =N-CH₂-CH₂-N=), 6.6 (s, 2H, H_c), 7.4 (s, 2H, H_d), 7.5 (s, 2H, H_e) and 12.0 (hump, 2H, enolic OH).

The infrared spectrum of the ligand shows a broad band in the range 3200-3000 cm⁻¹ which is assigned to intramolecularly hydrogen-bonded²⁰ -OH. The



(I)

spectrum displays strong absorption peaks at 1730, 1600 and 1230 cm^{-1} which are attributed to $\nu\text{C}=\text{O}$ (lactone carbonyl), $\nu\text{C}=\text{N}$ (azomethine group) and $\nu\text{C}-\text{O}$ (phenolic) respectively. A medium intensity band observed at 1000 cm^{-1} is assigned to $\nu\text{C}-\text{O}-\text{C}$.

In the infrared spectra of all the complexes no band is observed in the region 3200-3000 cm^{-1} which suggests the cleavage of intramolecularly hydrogen-bonded OH with subsequent deprotonation and coordination through phenolic oxygens. The $\nu\text{C}-\text{O}$ (phenolic) observed at 1230 cm^{-1} in the ligand shows a positive shift of 15-30 cm^{-1} , further confirming the involvement of deprotonated phenolic oxygen in complexation²¹. A negative shift in $\nu\text{C}=\text{N}$ of 20-25 cm^{-1} in all the complexes indicates the participation of azomethine nitrogen in coordination²². The presence of a broad trough in the region 3450-3050 cm^{-1} in the spectra of oxovanadium(IV), Mn(II), Fe(II), Co(II) and Cu(II) complexes suggests the presence of coordinated water which is further confirmed by the appearance of a non-ligand band in the region 820-830 cm^{-1} assignable to rocking mode of coordinated water²³. A strong band in oxovanadium (IV) complex was observed at 985 cm^{-1} which is

assigned to $\nu\text{V}=\text{O}^{22}$. New bands observed in the region 620-450 cm^{-1} are assigned to $\nu\text{M}-\text{N}$ and $\nu\text{M}-\text{O}$ modes²³. From the IR studies of the complexes it is presumed that the ligand AMUEN behaves in a dibasic tetradentate manner coordinating through the O:N:N:O donor sequence.

The presence of coordinated water is also established by TG and DT analyses. TG analysis of Mn(II), Fe(II), Co(II) and Cu(II) complexes shows that the mass loss per mole of the complex is equivalent to two moles of the coordinated water in a single step process and in case of oxovanadium (IV) complex the mass loss is equivalent to one mole of coordinated water. DT analysis of these complexes shows that the deaquation is a single step process. The endothermic peaks are obtained at 210, 196, 178, 150 and 162°C respectively.

The room temperature magnetic moment values and electronic spectral data are given in Table 1. The magnetic moment values for oxovanadium (IV) and Cu(II) complexes are consistent with the presence of one unpaired electron²⁴. Mn(II) complex shows a slightly low value when compared to spin-only value (5.92 B.M.). The low values may be due to the presence of Mn(III) species or spin-exchange in the solid phase¹³. The magnetic moment of Fe(II) complex agrees well with that expected for high-spin octahedral complexes²⁵. The high value (4.40 B.M.) for Co(II) complex may be due to orbital contribution²⁶. The Ni(II) complex is orange in colour and is diamagnetic which suggest a singlet ground term $^1A_{1g}$.

In the electronic spectrum of Mn(II) complex very weak absorption bands are observed which are not of

Table 1 - Analytical, Magnetic and Electronic Spectral Data of the Ligand and Complexes

Mol. formulae of the ligand and complexes	Found (Calc), %				$\mu_{\text{eff.}}$ (B.M.)	Electronic spectral bands (cm^{-1})	Tentative assignments
	Metal	C	H	N			
AMUEN	—	67.87	5.25	6.10	—	—	—
[C ₂₆ H ₂₄ N ₂ O ₆]	—	(67.82)	(5.21)	(6.08)	—	—	—
VO ²⁺ - AMUEN.H ₂ O	9.42	57.49	4.48	5.19	1.69	12600	$^2E_g \leftarrow ^2B_2$
[VC ₂₆ H ₂₄ N ₂ O ₈]	(9.38)	(57.46)	(4.42)	(5.15)	—	17850	$^2B_1 \leftarrow ^2B_2$
						27770	$^2A_1 \leftarrow ^2B_2$
Mn(II) - AMUEN.2H ₂ O	10.10	56.89	4.80	5.14	5.68	17850	
[Mn C ₂₆ H ₂₆ N ₂ O ₈]	(10.00)	(56.83)	(4.73)	(5.10)	—	19200	
Fe(II) - AMUEN.2H ₂ O	10.05	56.70	4.69	5.06	5.10	10500	$^5E_g \leftarrow ^5T_{2g}$
[FeC ₂₆ H ₂₆ N ₂ O ₈]	(10.15)	(56.74)	(4.72)	(5.09)	—	20833	Charge-transfer
Co(II) - AMUEN.2H ₂ O	10.58	56.37	4.68	5.01	4.40	8050	$^4T_{2g} \leftarrow ^4T_{1g}(F)$
[CoC ₂₆ H ₂₆ N ₂ O ₈]	(10.66)	(56.43)	(4.70)	(5.06)	—	21000	$^4T_{1g}(P) \leftarrow ^4T_{1g}(F)$
						28000	Charge-transfer
Ni(II) - AMUEN	11.39	60.43	4.29	5.46	Dia-	18500	$^1A_{2g} \leftarrow ^1A_{1g}$
[NiC ₂₆ H ₂₂ N ₂ O ₆]	(11.36)	(60.38)	(4.26)	(5.42)	magnetic	27700	$^1B_{1g} \leftarrow ^1A_{1g}$
Cu(II) - AMUEN.2H ₂ O	11.44	56.12	4.69	5.08	1.94	—	$\left\{ \begin{array}{l} ^2A_{1g} \leftarrow ^2B_{1g} \\ ^2B_{1g} \leftarrow ^2B_{1g} \\ ^2E_g \leftarrow ^2B_{1g} \end{array} \right.$
[Cu C ₂₆ H ₂₆ N ₂ O ₈]	(11.39)	(55.96)	(4.66)	(5.02)	—	14500	
						27770	Charge-transfer

any help in assigning the geometry. In the spectrum of Cu(II) complex a broad band is observed at 14500 cm^{-1} which is a combination of the three transitions given in Table I. In the case of other complexes the assignments agree with the proposed stereochemistries.

The ESR spectra show $g_{\parallel}$, $g_{\perp}$ and g_{av} values of 1.973, 1.950 and 1.958 respectively in the case of Cu(II) complex and 1.973, 1.945 and 1.954 respectively in the case of oxovanadium(IV) complex. The lower g values may be due to axial distortion tending to cubic symmetry because of symmetric environment of the ligand²⁷.

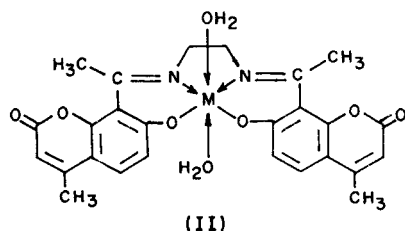
On the basis of magnetic data and electronic spectral studies oxovanadium(IV), Mn(II), Fe(II), Co(II) and Cu(II) complexes have been assigned octahedral geometries (structures II and III) while a square-planar

geometry is proposed for the Ni(II) complex (structure IV).

Our thanks are due to the Principal, Nizam College for providing necessary facilities; and one of us (PVR) is grateful to the CSIR, New Delhi for the award of senior research fellowship.

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Where M = Mn(II), Fe(II), Co(II) and Cu(II)

