

Synthesis & Structural Studies of Oxovanadium(IV), Manganese(II), Iron(II), Cobalt(II), Nickel(II) & Copper(II) Complexes of N-(4-Methyl-8-acetoumbel- liferonylidene)-N'-(isonicotinoyl)hydrazine

P VENKATESWAR RAO

Department of Chemistry, Nizam College, Hyderabad 500 001
and

N RAMA RAO & M C GANORKAR*

The Birla Institute of Scientific Research, Asmangadh Palace,
Malakpet, Hyderabad 500 036

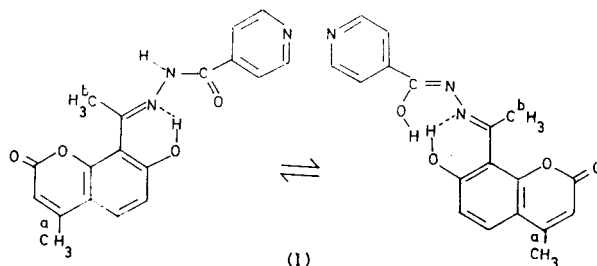
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Complexes of N-(4-methyl-8-acetoumbelliferonylidene)-N'-(isonicotinoyl)hydrazine [MAUINH] with oxovanadium(IV), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) have been synthesised and characterised on the basis of analytical, conductivity, magnetic moment, TG and DT, infrared, electronic and ESR spectral data. Metal to ligand ratio in all the chelates has been found to be 1:1. Infrared spectral data show that the ligand behaves in a dibasic tridentate manner in all the complexes except in Mn(II) complex where it acts as a monobasic tridentate ligand with O:N:O donor sequence. In Fe(II), Co(II) and Cu(II) complexes, the lactone carbonyl of the ligand (MAUINH) participates in coordination forming polymeric octahedral complexes. The Mn(II) complex has been assigned a dimeric octahedral structure with two chlorides acting as bridging centres between the metal ions. The Ni(II) and oxovanadium(IV) complexes have been assigned dimeric square-planar and square-pyramidal stereochemistries respectively.

In view of the promising physiological properties of coumarin and its derivatives¹⁻⁵, we report here the synthesis and characterisation of a new ligand, N-(4-methyl-8-acetoumbelliferonylidene)-N'-(isonicotinoyl)hydrazine (MAUINH), and its complexes with oxovanadium(IV), Mn(II), Fe(II), Co(II), Ni(II) and Cu(II).

4-Methyl-8-acetylumbelliferone was prepared by the reported method⁶. Isonicotinoyl hydrazide was a Fluka reagent. All the other chemicals used were of AR grade and the solvents were purified before use.

The ligand, MAUINH (I), was prepared by mixing 8-acetyl-4-methyl umbelliferone (4.36 g, 0.02 mol) with isonicotinic acid hydrazide (2.78 g, 0.02 mol) in 100 ml of ethanol. The pH of the reaction mixture was adjusted to 7-8 and it was refluxed for about two hours. On keeping the reaction mixture overnight, a light yellow crystalline product precipitated which was filtered, washed with ethanol and pet. ether (60-80°) and dried *in vacuo*.



The compound was recrystallised from dimethyl-formamide, m.p. 273°C.

[Found: C, 64.16; H, 4.60; N, 12.49. $C_{18}H_{15}N_3O_4$ requires: C, 64.10; H, 4.45; N, 12.46%]. IR: 3250 (ν NH), 3200-2800 (H-bonded ν OH)⁷, 1720 (ν C=O lactone), 1680 (ν C=O amide), 1600 (ν C=N)⁸, 1490 (ν C-O phenolic)⁹, 1060 (ν N-N) and 1020 cm^{-1} (ν C-O-C); PMR(DMSO- d_6): δ 2.3 (3H, s, a-CH₃), 3.7 (3H, s, b-CH₃), 6.5 (1H, s, C₃-H), 6.8-7.0 (1H, d, C₅-H), 7.6-8.0 (1H, d, C₆-H)¹⁰, 8.3-8.5 (1H, s, ArOH) and 12.7 (1H, s, enolic OH).

Preparation of the complexes

The metal complexes were prepared by mixing the ethanolic solutions of the ligand (0.01 mol) with the metal chlorides (0.01 mol); the pH of the reaction mixture was adjusted to ~ 8 and it was refluxed for 2-3 hr on a water bath. The metal chelates precipitated on refluxing the reaction mixture. The metal chelates thus precipitated were filtered, washed thoroughly with ethanol, followed by pet. ether (60-80°) and dried *in vacuo*.

All the physicochemical studies were carried out as described earlier⁶. The far infrared spectra of some of the complexes were recorded on a Polytech-FIR-30 IR spectrophotometer.

All the metal chelates are coloured, stable towards air and moisture, decompose at high temperatures and insoluble in common organic solvents, but sparingly soluble in DMF, DMSO and dioxane. The molar conductance values of these complexes (7-20 mhos $cm^2 mol^{-1}$) in DMF ($10^{-3} M$) show their non-electrolytic nature. The analytical data (Table 1) suggest that the metal to ligand stoichiometry is 1:1.

The absence of a broad band due to hydrogen bonded ν OH in the spectra of all the complexes suggests the cleavage of intra-molecularly hydrogen bonded -OH of the ligand with subsequent deprotonation and coordination through phenolic oxygen⁷. This is further supported by an upward shift in ν C-O (phenolic) to the extent of 15-20 cm^{-1} (ref. 11). In all

Table 1—Characterisation Data of the Complexes

Complex	Found (Calc.), %				$\mu_{\text{eff.}}$ (B.M.)	Electronic spectral data		
	Metal	C	H	N		λ_{max} (cm^{-1})	Dq (cm^{-1})	LFSE (kJ mol^{-1})
[Vo MAUINH] ₂	12.71 (12.67)	53.89 (53.74)	3.41 (3.23)	10.55 (10.45)	1.42	12800, 17000, 24000	1280	61.24
[Mn MAUINH·Cl·H ₂ O] ₂	12.41 (12.36)	48.28 (48.60)	3.52 (3.60)	9.48 (9.45)	5.16	8500, 15625, 27770	850	0
[Fe MAUINH·2H ₂ O] _n	13.12 (13.08)	50.68 (50.60)	4.06 (3.98)	9.96 (9.84)	5.10	10500, 28400	1050	50.24
[Co MAUINH·2H ₂ O] _n	13.62 (13.70)	50.10 (50.24)	4.02 (3.95)	9.90 (9.77)	4.60	8750, 18400	734.6	70.30
[Ni MAUINH] ₂	15.00 (14.91)	55.06 (54.86)	3.39 (3.30)	10.56 (10.67)	Diamagnetic	18520, 25000	1852	543.63
[Cu MAUINH·2H ₂ O] _n	14.69 (14.62)	49.52 (49.70)	3.98 (3.91)	9.75 (9.67)	1.86	15850, 27800	1585	113.75

*Satisfactory Cl analysis was obtained

the complexes, except Mn(II) complex, the ligand coordinates in its enolic form as shown by a strong band at 1580 cm^{-1} , which is diagnostic of azine ($>C=N-N=C<$) group¹², and the absence of the characteristic frequencies of $\nu C=O$ (amide). The presence of a band at $1240\text{--}1270\text{ cm}^{-1}$ suggests the participation of C—O (enolic) in complexation. In the spectra of Fe(II), Co(II) and Cu(II) complexes, a downward shift in $\nu C=O$ (lactone) frequency to the extent of 30 cm^{-1} suggests its involvement in coordination¹³. A negative shift in $\nu C=N$ to the extent of 20 cm^{-1} indicates the coordination of azomethine nitrogen¹⁴. This is further supported by an upward shift of 20 cm^{-1} in $\nu N-N$. The appearance of a broad crest in the region $3500\text{--}3200\text{ cm}^{-1}$ and a non-ligand band around 840 cm^{-1} in the spectra of Mn(II), Fe(II), Co(II) and Cu(II) complexes suggests the presence of coordinated water, which is further corroborated by TG and DT analyses.

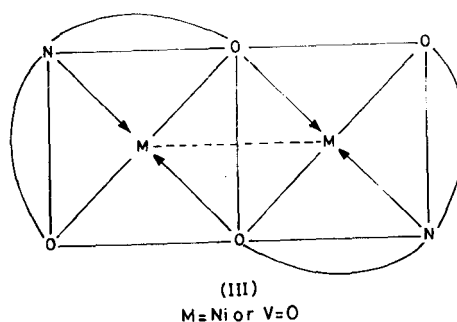
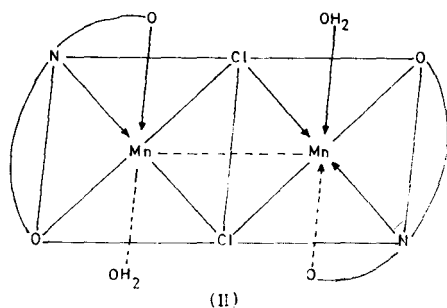
In the spectrum of Mn(II) complex the appearance of bands characteristic of νNH and $\nu C=O$ (amide) and the absence of the band due to $\nu C-O$ (enolic) suggest the coordination of the ligand in its keto form. The $\nu C=O$ (amide) undergoes a negative shift to the extent of 30 cm^{-1} which is a conclusive evidence of its coordination to the metal ion. A band observed at 240 cm^{-1} in the far infrared spectrum is due to $\nu M-Cl$ vibration which indicates the presence of a chloride bridge. This is supported by a low magnetic moment value and analytical tests¹⁵. The presence of enolic oxygen bridge in Ni(II) and oxovanadium(IV) complexes is substantiated by a positive shift in $\nu C-O$ (enolic) ($>25\text{ cm}^{-1}$)^{9,12}. A band at 980 cm^{-1} in the spectrum of oxovanadium(IV) complex can be assigned to $\nu V=O$. New bands observed in the region 300--

600 cm^{-1} in the spectra of all the complexes are attributable to $\nu M-N$ and $\nu M-O$ vibrations¹⁶.

Thermogravimetric analysis shows a single step mass loss equivalent to one mole of coordinated water per mole of the complex in Mn(II) and Fe(II) complexes and two moles of water per mole of complex in the case of Co(II) and Cu(II) complexes. This is further confirmed by one endothermic peak in DT analysis which occurs at 178, 192, 202 and 150°C for the Mn(II), Fe(II), Co(II) and Cu(II) complexes, respectively.

The room temperature magnetic moment values are given in Table 1. The magnetic moment values of oxovanadium(IV) and Mn(II) complexes are low when compared to the spin-only value, which may be due to the presence of antiferromagnetic interaction between the metal ions. This can be attributed to the dimeric nature of these complexes⁹. The magnetic moment values of Fe(II) and Co(II) complexes are well within the range of high spin octahedral complexes¹⁷.

The electronic spectral data are shown in Table 1. The electronic spectrum of oxovanadium(IV) complex exhibits three main absorption bands which are assigned to the three transitions ${}^2B_2 \rightarrow {}^2E$; ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ respectively in a square-pyramidal geometry¹⁸. The Mn(II) complex shows weak absorption bands which are not of any help in deciding the geometry. The first absorption band in Fe(II) complex is assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ transition and the other one to a charge-transfer transition. The Co(II) complex displays two main absorption bands which are assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)(\nu_1)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively. The ligand field parameters calculated¹⁸ for this complex are as follows: $B' = 699.6\text{ cm}^{-1}$; $\beta = 0.72$ and $\beta^\circ = 28\%$. These values show a



strong M – L covalent bonding in this complex. The Ni(II) complex shows two main absorption bands, which are assigned to $^1A_{1g} \rightarrow ^1A_{2g}$ and $^1A_{1g} \rightarrow ^1B_{1g}$ transitions, respectively in a square-planar disposition. The first absorption band in Cu(II) complex can be assigned to $^2E_g \rightarrow ^2T_{2g}$ transition and the other to a charge-transfer. The Dq and LFSE values (Table 1) show that the Cu(II) and Ni(II) complexes are more stabilised than the other complexes.

The ESR spectra of oxovanadium(IV) and Cu(II) complexes were recorded in the powder form at room temperature. The $g_{\parallel}$, $g_{\perp}$ and g_{av} values for these complexes are 2.004, 1.957 and 1.972; 2.145, 2.056 and 2.085 respectively¹⁹.

Based on the above data, it is proposed that the Fe(II), Co(II) and Cu(II) complexes are polymeric with octahedral geometries (IV) and Mn(II) complex is a chloride-bridged dimer in an octahedral stereochemistry (II). Ni(II) and oxovanadium(IV) complexes are dimeric with enolic oxygen bridged structures in square-planar and square-pyramidal geometries respectively (III).

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