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SYNTHESIS AND CHARACTERIZATION OF NITROACYL-5-OXO-PYRAZOLE AND ITS VANADIUM(V), IRON(III) AND COBALT(II) COMPLEXES

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ABSTRACT. The synthesis and characterization of 3-methyl-4-(*p*-nitrobenzoyl)-5-oxo-1-phenylpyrazole and its Fe(III), Co(II) and V(V) complexes are described. The structures of the complexes and the mode of chelation were established by elemental analyses, UV-visible, IR and ^{1}H and ^{13}C NMR spectral studies. The studies suggest that the ligand and metal ions form neutral complexes of general formula $M(Npy)_n.X$. (Npy = ligand anion). X is an adduct in which Fe(III) forms tris(1-phenyl-3-methyl-4-acylpyrazolonate)iron(III)monohydrate, $Fe(NPy)_3.H_2O$ and Co(II) forms a diaquobischelate, $Co(NPy)_2.2H_2O$, while V(V) forms a dioxo adduct chelate, $VO_2(NPy).HNPy$.

INTRODUCTION

The chemistry of transition metal complexes with 4-acyl-5-oxo-pyrazoles and other 5-oxo-derivatives have been studied [1]. The interest shown in these groups of metals result from their spectral and magnetic properties. Several complexing reagents have been suggested for their extraction from aqueous media [2-6]. The use of 4-acyl-oxo-pyrazoles has been dominant. However, most of the work on the metal complexes of these reagents has been concerned with other substituted derivatives of the 1-phenyl-3-methyl-5-oxo-pyrazole moiety [5,7]. Fewer reports have appeared on the use of the nitro derivatives. In our earlier communications [8], we have reported the extraction separation of U(VI), Fe(III), Ni(II), Co(II) and Cu(II) using the nitro derivatives.

Our investigations on metal complexes [9] are being extended to the preparation and spectroscopic studies of the Fe(III), Co(II) and V(V) complexes to understand the mode of interaction between the metals and the ligand in aqueous media. This paper reports the results of microanalyses, molar conductivities, and the spectral investigations of the nitroacyl-oxo-pyrazole and its metal complexes (Figures 1a and 1b, respectively).

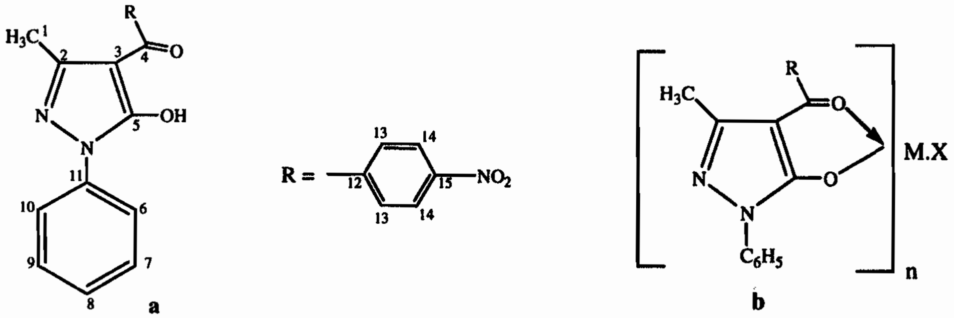

Figure 1. Structure of (a) ligand and (b) metal complexes (M = V, Fe, and Co; X = H_2O for Fe and Co, and HNPy for V; n = 3 for Fe and 2 for V and Co).

EXPERIMENTAL

Reagents. Analytical grade reagents from BDH, Aldrich or Merck were used. They include ethylacetoacetate, phenylhydrazine, *p*-nitrobenzoyl chloride, iron(III) ammonium sulphate, ammonium vanadate, and 95% ethanol. Distilled demineralized water was used in all the experiments. The ligand was synthesised as described by Okafor *et al.* [7] and Jensen [10] for pyrazolones.

Preparation of metal complexes. The Fe(III), Co(II) and V(V) solutions were prepared by dissolving respectively 0.81 g (1.68 mmol) $NH_4Fe(SO_4)_2.12H_2O$, 0.625 g (2.5 mmol) $Co(CH_3COO)_2.4H_2O$ and 0.3 g (2.5 mmol) NH_4VO_3 in 50 mL of water with warming. Each solution was added dropwise with stirring to a hot 75 mL ethanol solution of 1.62 g (5.0 mmol) of the complexing agent. This gave a complex of metal-ligand mole ratio of 1:2 for Co(II) and V(V) and 1:3 for Fe(III). The iron(III) complex precipitated out instantly while those of Co(II) and V(V) came out gradually on cooling of solutions.

The crystalline product in each case was washed with aqueous ethanol (1:1), filtered, air-dried and stored over fused calcium chloride in a desiccator. The metal complexes are characterized by the general formula given in Figure 1b.

Physical measurements. Infrared spectra (4000-400 cm^{-1}) were obtained on a Nicolet 510 FT-IR spectrometer. All samples were prepared as transparent KBr pellets using a tenton Carver press. UV-visible spectra were recorded on a Pye Unicam SP8-100 spectrophotometer. Proton and carbon-13 NMR spectra were obtained on a Varian Gemini-200 IH FT Spectrometer operating at field strength of 4.7 Tesla (at 200 and 50.3 MHz for ^1H and ^{13}C, respectively). Chemical shifts are reported in δ ppm relative to TMS as internal standard.

All the samples were soluble in acetone-d_6, which was the solvent used for all NMR investigations. All the samples except the Fe(III) complex were insoluble in $CDC1_3$. An electrothermal apparatus was used for determining the melting points of all compounds, while magnetic susceptibility measurements were made with a Johnson Mathey Chemical Balance. Micraonalyses were performed for C, H and N on all the compounds.

RESULTS AND DISCUSSION

Analytical data, including elemental analyses and some physical properties of the ligand and metal complexes are listed in Table 1. They indicate that the enolised ligand (Figure 1a) and metal complexes (Figure 1b) were synthesized, and that in aqueous solution the mode of interaction between the ligand and metal ions is in the mole ratio of 1:2 for V(V) and Co(II), and 1:3 for Fe(III). The complexes conform to the general molecular formula, $M(NPy)_nX$, where n is the oxidation state of the metal (M) and the ligand number, and X is H_2O for Fe(III) and Co(II), and HNPy for the V(V) complex. The chelation process leading to the formation of metal complexes can thus be formulated as displacement of protons from ligand molecules:

$$M^{n+}_{(aq)} + nHL_{(org)} \rightleftharpoons ML_{n(org)} + nH^{+}_{(aq)}$$

Solubility data shown in Table 2 indicate that the ligand and Fe(III) complex are remarkably soluble both in polar solvents (except water and ethanol) and non-polar solvents. The V(V) and Co(II) complexes have low solubility in organic solvents such as carbon tetrachloride, chloroform, toluene, benzene and cyclohexane. The adducts in the V(V) and Co(II) complexes probably complete the octahedral coordination sphere. This could be responsible for their solubility in polar solvents such as DMSO, benzyl alcohol and acetone. Conductivity measurements in acetone (10^{-3} M complex) show negligible molar conductance values for the complexes, showing them to be non-ionic compounds.

Table 1. Some physical and microanalytical data for ligand and metal complexes.

Compound	Molecular formula	Colour	m.p. (°C)	Yield (%)	% Found (% calcd) C	H	N
HNPy	$C_{17}H_{13}N_3O_4$	Orange	165	91	63.46(63.19)	4.00(4.06)	13.08(13.01)
$Fe(Npy)_3.H_2O$	$FeC_{51}H_{30}N_9O_{12}$	Wine red	286	97	59.15(59.20)	3.35(3.12)	12.10(12.18)
$Co(Npy)_2.2H_2O$	$CoC_{35}H_{28}N_6O_{10}$	Yellow	185	82	55.88(55.93)	11.02(11.20)	11.08(11.20)
$VO_2(NPy).HNPy$	$VC_{35}H_{25}N_6O_{10}$	Whitish yellow	242	78	56.64(56.78)	3.10(3.40)	11.50(11.35)

Table 2. Solubility data for HNPy and metal complexes.

Solvent	HNPy	V(V) complex	Fe(III) complex	Co(II) complex
Water	is	is	is	is
Ethanol	ss	is	is	is
Acetone	vs	s	vs	vs
Xylene	s	is	ss	is
Toluene	vs	is	vs	is
Benzene	vs	is	vs	is
Cyclohexane	is	is	is	is
Benzylaclcohol	vs	vs	vs	vs
Carbon tetrachloride	ss	is	is	is
Chloroform	vs	ss	vs	ss
Dioxan	vs	vs	vs	vs
DMSO	vs	vs	vs	s
Ethylacetate	vs	vs	vs	vs
Diethyl ether	vs	s	vs	vs
Propan-2-ol	s	s	s	s

Key: is = insoluble, ss = slightly soluble, s = soluble, vs = very soluble.

Electronic spectra. The electronic spectral data of the ligand and its metal complexes are given in Table 3. The ligand and its metal complexes have virtually identical spectra in the near UV region (λ_1 = 360 nm for the ligand, 370 nm for Fe(III), 368 nm for V(V) and for Co(II). These data suggest that the π-bonding system in 4-nitroacyl-oxo-pyrazole is almost intact in the ligand anion of the metal complexes [5,7,11,12]. Absorptions at these regions are therefore ascribed to $\pi \rightarrow \pi^*$ transitions. The inference from this is that there is no interaction between the π-bonding system of the ligand and the M^{n+} ions. The interactions between metal ions and the ligand is mainly through σ-bond formation between M^{n+} ions and the oxygen atoms of the C=O groups of the ligand.

The broad absorption band between 430 nm and 550 nm observed for the Fe(III) complex is assigned to ligand→metal charge transfer. Similar bands have been reported for Fe(III) complexes of 4-acyl-oxo-pyrazoles [6,12]. Bands due to d→d transitions are not commonly observed for Fe(III) complexes because for high-spin d^5 configuration all d→d transitions are both symmetry and spin-forbidden. The higher molar absorptivities of the chelates and the observed bathochromic shifts at λ_1 (360-370 nm) bands of the M^{n+} complexes indicate chelate formation between M^{n+} ions and Npy^- anions. The bands due to d→d transitions in Co(II) and V(V) were obscured by the more intense π→π* bands and could not be observed.

Table 3. Electronic spectral data and the molar conductance for HNPy and metal complexes in acetone.

Compound	λ_{1max} (nm)	ε_1 $L.mol^{-1}cm^{-1}$	λ_{2max} (nm)	ε_2 $L.mol^{-1}cm^{-1}$	Molar conductance $S.mol.^{-1}cm^{-1}$
HNPy	360	5.4×10^2	-	-	-
V-NPy	368	3.0×10^3	-	-	6.3
Fe-NPy	370	2.5×10^4	480	1.4×10^4	5.8
Co-NPy	368	3.3×10^3	-	-	5.2

Infrared spectra. The observed IR frequencies have been assigned by comparison with those of previous reports on 4-acyl-oxo-pyrazoles and their metal complexes [3,5-7,11-15]. The IR absorption spectra have been divided into three main spectral regions: 4000-1800, 1800-1000, and 1000-400 cm^{-1}. The IR spectral data are shown in Table 4.

4000 -1800 cm^{-1} region. The strong but broad band at 3114 cm^{-1} of the ligand is assigned to the νO-H frequency of the enol. A strong band centred at 2524 cm^{-1} for the V(V) complex is typical of -OH----O bands arising from the vibrations of -OH of the enol-keto form of 1,3-diketones involved in intramolecular hydrogen-bonding. The band at 3114.30 cm^{-1} for the V(V) complex is assigned to the stretching frequency of -OH group of the coordinated neutral HNPy adduct. Similar observations have been previously noted by Hallam [16], Okafor [7,11] and Uzoukwu [5,6]. The νOH----O band is absent in the IR spectra of the Fe(III) and Co(II) complexes. These facts indicate deprotonation of the -OH group during chelation, and the formation of M-O bonds in place of -OH bonds in the metal complexes. The broad absorption band centred at 3555 cm^{-1} region of the IR spectrum of the Co(II) complex has been assigned to the νO-H of the coordinated water molecule, while that near 3441 cm^{-1} for the Fe(III) complex is ascribed to the O-H stretching frequency of water in the crystal lattice. IR spectra of the Fe(III) complex run in three different laboratories revealed the same spectral features, and were confirmed by elemental analyses. From all available literature, Fe(III) does not seem to exceed a coordination number of six with acyl-oxo-pyrazolones [3,6,7]. This supports the view that the water molecule in the Fe(III) complex resides outside the primary coordination sphere of the complex. It is perhaps trapped in the crystal lattice during crystallization.

1800-1000 cm^{-1} region. Most of the bands observed in this region are attributable to oscillations of the oxo-pyrazole chelate rings. Normal coordinate calculations [13,14] and isotopic studies [6,17] on β-diketones showed that νC=O occurs at a higher frequency than νC=C. Hence, the absorption bands occuring at 1686 and 1594 cm^{-1} for HNPy, 1688 and 1609 cm^{-1} for Fe(III), and 1608 cm^{-1} for Co(II) have been assigned to the C=O and C=C stretching frequency modes, respectively.

The shift of νC=O from 1686 cm^{-1} in the IR spectrum of HNPy to very strong (except iron) absorption bands in the 1600-1608 cm^{-1} region of the IR spectrum of the Fe(III) and Co(II) complexes, and 1688 cm^{-1} for the V(V) complex, assigned to ν_{as}C=O, suggests that the carbonyl group is involved in coordination with the metal ions. The large bathochromic shifts of about 86 cm^{-1} in the Fe(III) and Co(II) complexes indicate stronger M-O bonds in these metal complexes than in the V(V) complex with very low hypsochromic shifts of only about 2 cm^{-1}. The bands near 1509 and 1530 cm^{-1} are due to ν_{as}C=C=C of the metal complexes. The involvement of C-O and the pyrazole carbon (labelled 3,4,5) systems in coordination with M^{n+} ions through electron delocalization (Figure 1b) is supported by the shift of bands assigned to ν_{as}C=C=C from 1550 cm^{-1} in the ligand by about 40-84 cm^{-1} in the metal complexes.

The observed absorption bands between 1075 and 1078 cm^{-1} have been ascribed to C-H in-plane-deformation of the phenyl ring in the complexes. Comparison with the spectrum of the ligand also shows that there is little or no shift (except for the V(V) complex) in the above frequencies. This further supports the suggestion that the π-bonding system of the mono-substituted phenyl ring of the free ligand is not involved in coordination with the M^{n+} ions.

Table 4. The IR spectral data for ligand and metal complexes and approximate assignments.

HNPy	V(V) complex	Fe(III) complex	Co(II) complex	Assignments
		3441 b	3555 b	νO-H of water
3114 b	3114 m	-	-	νO-H of enol
2844 b	2968 b	3072 w	3064 b	νC-H
2524 m	2542 m	-	-	νO-H---O
1900 w	1975 w	2375 w	-	βO-H of water
1686 vs	-	-	-	νC=O of ligand
-	1688 vs	1600 w	1608 vs	ν_{as}C=O
1550 vs	1510 vs	1465 s	1487 vs	ν_{as}C=C=C
1416 vs	1443 s	1388 w	1400 w	$\beta_{as}CH_3$
1337 vs	1249 vs	1344 vs	1344 vs	ν_sC=O
1281 vs	1200 m	1183 m	1239 w	ν_sC=C=C
1200 m	-	-	-	βC-H
1100 m	1116 s	1116 w	1136 w	βC-H
1075 w	1033 m	1078 m	1075 m	C-H in-plane deformation of mono-substituted phenyl ring
925 s	983 w	1025 m	1016 m	CH_3 rocking
-	884 s	966 m	950 m	ν_{as}O=M=O
883 s	916 vs	-	-	γC-H
800 s	800 s	833 m	840 m	γC-H
725 vs	-	766 m	766 m	γC-H
705 vs	713 vs	716 m	716 m	Chelate deformation
-	691 w	658 w	666 w	Chelate deformation
-	645 w	633 m	616 m	Chelate deformation
-	633 w	591 w	583 w	Chelate deformation
-	633 w	591 w	583 w	Chelate ring vibrations
-	600 w	-	-	Chelate ring vibrations
566 m	563 m	-	575 w	Chelate ring vibrations
525 s	533 m	525 w	541 w	Chelate ring vibrations
-	483 w	466 w	466 w	ν(M-O + chelate ring)
450 w	445 w	-	-	ν(M-O + chelate ring)
-	416 w	400 w	400 w	νM-O

Legend: s-strong, m-medium, b-broad, s-very strong, ν-stretching frequency, ν_s-symmetric stretching, ν_{as}-asymmetric stretching frequency, β-bending or deformation, $_s$ γ-out-of-plane bending.

1000 - 400 cm^{-1} region. The frequency bands of interest in this region are those attributable to the vanadyl ion (VO_2^+) and to metal-ligand and chelate ring vibrations [6,7,18]. The strong absorption band at 916 cm^{-1} (VO_2^+) is thus ascribed to ν_{as}O=V=O, while the unique absorption bands between 700 and 600 cm^{-1} are due to chelate and metal-oxygen vibrations that are absent in the spectrum of the ligand. The absence of these bands in the IR spectrum of the ligand indicates chelation. The presence of bands between 600 and 400 cm^{-1}, which are typical of 1,3-diketonates, have been suggested as due to bonding to metals through the oxygen atom of the ligand [11,15,19]. The weak bands in the IR spectra of the metal complexes appearing at 416 cm^{-1} (V) and 400 cm^{-1} (Co and Fe) have been assigned to νM-O. The M-O stretching frequencies for the chelates follow the pattern: V > Fe ≅ Co. The higher melting point for the Fe(III) complex than for other metal complexes could be attributed to extra stability associated with an extra chelate ring.

NMR spectra. The simplicity of the NMR spectra of the ligand and the vanadium(V) complex permitted the general assignments of the ^{1}H and ^{13}C resonance signals to be made as labelled in Figure 1a. All ^{1}H and ^{13}C NMR assignments shown in Tables 5 and 6 were made by comparison with published reports [3,6,7,12,20] on ^{1}H and ^{13}C NMR spectral properties of 4-acyl pyrazoles and their metal complexes. The resonance signals and their assignments lend support to the structure shown in Figure 1b. For all the ^{1}H spectra, the quintet at 2.07 ppm is from the solvent acetone-d_6. The Fe(III) and Co(II) complexes did not show any proton (0-20 ppm) or carbon-13 (0-300 ppm) signals. This is due to large paramagnetic shifts usually observed with these metals. The singlet peak in the ^{1}H NMR spectra at 2.40 ppm in both ligand and V(V) complex is ascribed to methyl protons, while the multiplets between 8.25-8.39 ppm (C_6-C_{10}) and 7.38-8.04 ppm (C_7-C_{14}) appearing downfield in the spectrum of the V(V) complex are attributed to phenyl protons. The existence of resonance peaks between 7.38 and 8.04 ppm in the V(V) complex that are absent in the ligand indicate that V(V) and HNPy are involved in chemical reaction.

Table 5. Proton NMR chemical shifts δ ppm relative to TMS in acetone-d_6.

Proton no.	1	6 and 10	7-9	13	14
HNPy	2.43 (s)	8.25-839 (m)	-	-	-
V-NPy	2.40 (s)	8.27-8.47 (m)	7.87-8.04 (q)	7.55 (t)	7.38 (t)

Legend: s-singlet, t-triplet, q-quartet, m-multiplet

The ^{13}C NMR spectral data for the ligand and V(V) complex are shown in Table 6 together with the assignments made. The C(1) and C(3) resonance signals in the V(V) complex appear upfield relative to the signals for the ligand. In addition to these, the C(5) atom of the V(V) complex also resonates downfield from that of HNPy. This is probably due to the involvement of these carbon atoms in the chelation process through electron delocalization [8] as depicted in Figure 1b.

Table 6. ^{13}C NMR chemical shifts in δ ppm relative to TMS in acetone-d_6.

Carbon no.	1	2	3	4	5	6	7	8	9	10	11
HNPy	-	149.10	76.5	204.24	163.85	122.25	129.61	125.75	129.61	122.25	134.74
V-Npy	15.90	150	106	204.24	164.05	122.53	129.84	-	109.84	122.53	134.76

Magnetic moment data. Vanadium(V) with electronic configuration [Ar].$3d^0$, is diamagnetic and its complex VO_2(NPy).HNPy has a zero magnetic moment. The Fe(III) complex with t^3_{2g} e^2_g configuration is paramagnetic with an observed effective magnetic moment of 5.04 BM at 300 K. The theoretical spin-only value of 5.92 BM is expected for an octahedral, high-spin Fe(III) complex, a weakly paramagnetic low-spin Fe(III) complex is expected to have a theoretical spin-only value of 1.73 BM. The magnetic moment of 5.04 BM for the iron complex is somehow close to the theoretical spin-only value of 4.90 BM for an Fe(II) complex from reduction of Fe(III) to Fe(II) by the acylpyrazolone had occurred. However, micro-analytical data showed Fe(Npy)$_3$.H_2O to be produced, and that reduction from Fe(III) to Fe(II) did not occur. The deviation of the observed magnetic moment from the theoretical spin-only value (5.92 BM) could be an indication of some degree of distortion from regular octahedral symmetry in the Fe(NPy)$_3$ structure.

Magnetic moment values in the range 2.1-2.9 BM for Co(II) complexes are exhibited by low-spin square planar Co(II) complexes [21-23], whereas values in the range 4.2-4.7 BM are attributed to tetrahedral, and 4.8-5.6 BM to high-spin octahedral Co(II) complexes [21-23]. The observed magnetic moment value of 4.96 BM is suggestive of an octahedral structure for the Co(II) complex and perhaps a pseudo-octahedral geometry.

CONCLUSION

The combination of data from elemental analysis, magnetic moment, electronic, IR and NMR studies show that the 4-oxo-pyrazole forms neutral complexes with the metal ions, and that their structures conform to the types shown in Figure 1b. The results also suggest distorted octahedral configurations for the Co(II) and the Fe(III) complexes, in which water molecules take up two positions of the octahedron in Co(II), while Fe(III) complex is coordinatively saturated with ligand molecules. Vanadium(V) forms a coordination complex with a free ligand adduct. The bonds between HNPy and a metal ion are formulated as σ-bonds formed through the carbonyl and hydroxyl groups of the keto-enol form of the ligand.

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