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STUDIES ON THE COORDINATION COMPLEXES OF CALCIUM(II), CADMIUM(II) AND TIN(IV) WITH *p*-NITROBENZOYL-5-OXO-PYRAZOLE

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ABSTRACT. Complexes of Ca(II), Cd(II) and Sn(IV) with *p*-nitrobenzoyl-5-oxo-pyrazole (HNP) have been synthesized. The complexing agent and the metal complexes were characterized by elemental analyses, and UV-visible, IR and NMR spectroscopies. The results are consistent with the chemical formula, $M(NP)_2.nH_2O$ (M = Ca and Cd, and n = 2), and $M(NP)_2(OH)_2$ for Sn(IV). The study indicates the formation of neutral 6-membered coordination complexes by the metal ions and HNP anions. Octahedral bischelate complexes are presumed to be formed through the enolic and carbonyl oxygen atoms of the coordination reagent, in which water molecules and hydroxo ions complete the expected coordination numbers of Ca(II) and Cd (II), and Sn(IV), respectively.

INTRODUCTION

The interaction between 4-acyl-oxo-pyrazoles with various metal ions in aqueous solutions to form coordination complexes which can be extracted [1-5] or isolated in the solid state [6-10] have been studied. Because the 4-acyl-oxo-pyrazoles form highly stable metal chelates that are principally hydrophobic, they have found applications as extractants for metals from aqueous solutions, and also as strong active ingredients in analgesic, antihistaminic and antifungal formulations [11, 12]. Attempts at using other derivates of oxo-pyrazoles on constructing mixed ligand resins for trapping toxic metals chromatographically have been made [13, 14].

The potential applications of 4-acyl-oxopyrazoles in medicine, in the extraction and construction of ion-exchange resins for metal ions are some of the obvious incentives behind the investigation of the interaction between metal ions in solution and the cheating agent. However, many reagents of this type have appeared in the literature for the extraction of metals and formation of solid complexes [5-6] of many metals, but less attention has been paid specifically, to the use of nitroacyl-oxo-pyrazoles. The present study was undertaken to examine the mode of interaction between these metals and the cheating agent, HNP, in aqueous solutions, as well as the physical and spectroscopic properties of the complexes.

EXPERIMENTAL

Reagents and equipment. The synthesis of the complexing reagent (HNP) was performed according to the method of Jensen [15], by the reaction of 3-methyl-5-oxo-1-phenylpyrazole with the corresponding acylchloride [6], the *p*-nitrobenzoyl chloride. Distilled demineralized water was used in all reagents and experiments requiring water. Other reagents used included $Ca(CH_3COO)_2$, $CdCl_2.2H_2O$, $SnCl_4.5H_2O$ and 95% ethanol. Analar grade reagents were used in all cases.

The UV-visible measurements were obtained on a Pye Unicam SP8-100 spectrophotometer, while IR Spectra were recorded on a Nicolet 510 FT-IR spectrophotometer over the range 4000 - 400 cm^{-1}. All samples were prepared as transparent KBr pellets using a tenton carver press. ^{1}H and ^{13}C NMR spectra were obtained on a Varian Gemini - 200 IH FT spectrometer at 4.7 Tesla (at 200 and 50.3 MHz for ^{1}H and ^{13}C, respectively). Chemical shifts are reported in δ relative to TMS as internal standard. All samples are soluble in acetone and acetone-d_6, and were respectively used for all UV-visible and NMR measurements. Electrothermal apparatus was used for melting point determinations. Microanalyses were performed for C, H and N on all the compounds.

Preparation of metals complexes. The complexes of Ca(II), Cd (II) and Sn(IV) with HNP were prepared by dissolving 5 mmol 0.908 g) of $Ca(CH_3COO)_2$ and 5 mmol (1.30 g) of $CdCl_2.2H_2O$, respectively, in 100 mL warm water. Each of the Ca(II) and Cd(II) solutions was added dropwise with stirring to a 100 mL hot ethanol solution of 10 mmol (3.23 g) HNP, giving a metal-ligand mole ratio of 1:2 for the Ca(II) and Cd(II) complexes. For Sn(IV) complex, 2.5 mmol (0.88 g) $SnCl_4.5H_2O$ dissolved in 0.1 M HCl were treated as above with 10 mmol (3.233 g) HNP ethanol solution to give a metal : ligand mole ratio of 1:4. In all cases, the mixed solution was heated up to 60°C and allowed to cool to room temperature, whereby the voluminous (for Ca and Cd) precipitates appeared. The precipitate was filtered, washed with aqueous ethanol (2:1), and left in a desiccator to dry, giving fine crystals. For the case of Sn(IV) - ligand complexation reaction, some excess unreacted HNP was observed, which floated on top of the supernatant layer, and was decanted.

RESULTS AND DISCUSSION

The physical and chemical data shown in Tables 1 to 5 are consistent with the chemical formula proposed for the respective compounds. They show that the enolized ligand (Figure 1) and dihydrous bischelate metal complexes are synthesized for Ca(II) and Cd(II), and a dihydroxo bischelate complex for Sn(IV). The stoichiometries of the complexes show 1:2 ligand-metal ratio conforming to the general formula, $M(NP)_2.2H_2O$, for Ca(II) and Cd(II), and $M(NP)_2(OH)_2$ for Sn(IV).

The ligand and metal complexes are hydrophobic and sufficiently soluble in acetone, acetylacetate, diethylether, and higher alcohols, and produce solutions that have negligible molar conductance. The advantage of these organic solvents is that the solvent molecules possess lone pairs of electrons for possible donation, and can therefore, be used in conjunction with some other inert organic solvents such as $CHCl_3$ and CCl_4 for their extraction from aqueous solutions, and more particularly, for those metals that form hydrated complexes which do not have all the coordination sites saturated by the organic reagents [4, 5, 16, 17].

It is obvious that the presence of excess ligand at the end of complexation reaction for Sn(IV) may probably imply that not all the reagents took part in the coordination reaction. This is perhaps due to competitive hydrolysis reaction and polarization effect of highly charged Sn(IV) ion on water molecules, resulting in the formation of a dihydroxo bischelate Sn(IV) complex. The transition from aquo- to hydroxo-ligand is facilitated by the high formal charge on the metal ion, so that on polarization of water molecules, OH^- ions are formed which took up some of the coordination sites meant for NP^- anions.

Table 1. Some physical and elemental analyses data of HNP and Ca(II),Cd(II) and Sn(IV) complexes.

Compound	Molecular formula	Colour	Yield (%)	Melting point, °C	% Found (calcd)		
					C	N	H
HNP	$C_{17}H_{13}N_3O_4$	Orange	89	165	63.05 (63.15)	13.00 (12.96)	4.18 (4.12)
$Ca(NP)_2.\ 2H_2O$	$CaC_{34}H_{28}N_6O_{10}$	Bone white	96	226	46.15 (46.32)	9.50 (9.50)	3.30 (3.20)
$Cd\ (NP)_2.2H_2O$	$CdC_{34}H_{28}N_6O_{10}$	Brownish yellow	98	231	42.91 (42.80)	8.90 (8.81)	2.90 (2.91)
$Sn(NP)_2.(OH)_2$	$SnC_{34}H_{26}N_6O_{10}$	Yellow	86	310	42.58 (42.60)	8.71 (8.77)	2.74 (2.73)

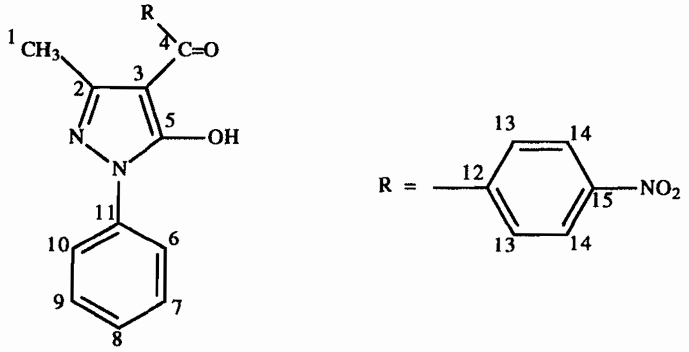

Figure 1. Structure of ligand .

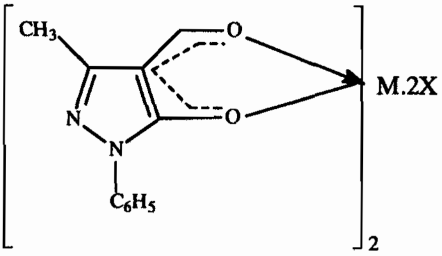

Figure 2. Metal complexes (M = Ca, Cd, and Sn; X = H_2O for Ca and Cd, and OH for Sn).

Thus;

$$Sn(H_2O)_4^{4+}(aq) \rightarrow Sn(H_2O)_2(OH)_2^{2+}(aq) + 2H^+\ (aq)$$

The competitive reaction probably left some of the HNP unreacted.

$$Sn(H_2O)_2(OH)_2^{2+} + 2HNP \rightarrow Sn(NP)_2(OH)_2 + 2H^+$$

Electronic spectra. Table 2 gives the electronic spectral data of HNP and the metal complexes dissolved in acetone. As revealed in the table, the ligand and the metal complexes appear to have virtually identical spectra, and absorb in the near visible region around λ_1 = 360 nm for the ligand and 365 nm for Ca(II), 368 nm for Cd(II) and 336 nm for Sn(II) complexes. These absorption are ascribed to intraligand $\pi \rightarrow \pi^*$ transitions. The almost identical spectra of HNP and the metal complexes suggests that the π-bonding system of the free nitroacyl-oxo-pyrazole is almost intact in the ligand anion of the metal complexes [6, 7, 19], indicating that there is no interaction between the metal ions and the π-bonding system of ligand. The coordination between NP^- and metal ions is therefore, through σ bond formation between metal ions and the O atom of the carbonyl group of the ligand as shown in Figure 1 and 2.

Table 2. UV - visible spectral data for HNP and its Ca(II)Cd (II) and Sn(IV) complexes.

Compound	$\lambda_{1\,max}$ (nm)	ε_1 (L. mol^{-1} cm^{-1})	$\lambda_{2\,max}$ (nm)	ε_2 (L. mol^{-1} cm^{-1})
HNP	360	540		
Ca - NP	365	1600		
Cd - NP	368	2100		
Sn - NP	336	1100	346	2800

Infrared spectra. The IR spectral data for the ligand and metal complexes are listed in Table 3. The observed IR frequency modes have been assigned by comparing with published reports on 4-acyl-oxo-pyrazoles and their metal complexes [6-10, 14] and other structurally related compounds [20, 21, 22]. The broad absorption band that appear at 3114 cm^{-1}, which is absent in the spectra of metal complexes is assigned to νOH of the enol form of the ligand, while the band around 2524 cm^{-1} for HNP, and the satellite but broad peaks between 2800 and 2545 cm^{-1} for the metal complexes are ascribed to the νOH---O frequency, and are typical of β-diketones and diketonates involved in intramolecular hydrogen bonding. Similar observations have been reported by Okafor *et al.* [6,7],

Taygari *et al* .[10], and Uzoukwu [18]. However, the broad bands appearing in the 3421-3474 cm^{-1} of the IR spectral region for the metal complexes have been attributed to νOH of adduct water molecules coordinated to the central metal ion or residing in the crystal lattice of the complexes [6, 18, 21, 23, 24]

The band centered around 1685 cm^{-1} in the IR spectrum of the ligand is assigned to symmetric carbonyl vibrations, νC=O. The assignments also show a shift of the νC=O from 1685 cm^{-1} recorded for HNP, to strong bands appearing at higher frequencies at 1693 cm^{-1} (Ca), 1693 cm^{-1} (Cd) and 1687 cm^{-1} (Sn) for the metal complexes, suggesting that: (i) C=O is involved in chelation, and (ii) the chelation process is essentially that of displacement of H ions of the ligand by the metal ion, and the formation of the C=O -M bonding system by the reaction of the type:

$$M^{n+}(aq) + nHNP(org) \rightarrow M(NP)_n(org) + nH^+ (aq)$$

where n is the number of ligands involved.

Table 3. IR spectral data for HNP and Ca(II),Cd (II) and Sn(IV) complexes.

HNP	Ca-NP	Cd-NP	Sn-NP	Assignment
-	3474 b	3428 sh	3421 sh	νOH of water
3114 b	-	-	-	νOH of enol
2984 b	3058 b	3057 b	3039 b	νC-H
2844 m	2845 m	2766 m	2766 w	νOH---O
2524 m	2545 w	2545 m	2583 w	νOH---O
1900 w	1975 w	1945 w	-	βOH of water
1685 vs	-	-	-	νC=O
-	1693 vs	1693 vs	1686 s	ν_{as}C=O
1595 vs	1614 vs	1614 vs	1615 vs	Phenyl ring νC=C
1550 vs	1529 vs	1529 s	1516 vs	ν_{as}C=C=C
1416 vs	1441 m	1441 s	1414 m	$\beta_{as}CH_3$
-	-	-	1400 m	$\beta_{as}CH_3$
1337 vs	1344 vs	1344 vs	1338 vs	ν_sC=O
1281 vs	1281 s	1281 vs	1282 m	ν_sC=C=C
1220 m	1216 m	1216 m	1224 m	βC-H
1100 m	1116 m	1133 m	1116 m	
1075 w	1016 w	1016 w	1026 w	C-H deformation of phenyl ring
925 m	950 s	940 m	-	CH$_3$ rocking
883 s	883 m	833 m	875 m	CH$_3$ rocking
800 s	-	-	-	CH$_3$ rocking
725 vs	758 w	728 vs	756 w	γC-H
705 vs	705 s	705 s	705 vs	γC-H
-	591 w	600 w	600 w	ν(M-O + chelate ring vibrations)
-	583 w	583 w	566 w	ν(M-O + chelate ring vibrations)
525 s	533 m	526 m	530 w	ν(M-O + chelate ring vibrations)
450 w	441 w	450 w	-	νM-O
-	416 w	433 w	-	νM-O

s, strong; b, broad; m, medium; sh, shoulder; vs, very strong; ν, stretching frequency; ν_{as}, asymmetric stretching frequency; β, bending or deformation; ν_s, symmetric stretching frequency; γ, out of plane bending.

Bands due to νC=C are known to be very sensitive to chelation in β-diketones [6,7,24]. The indication of the involvement of the -C=C- of the oxo-pyrazole bonding system in chelation through electrons delocalization of the chelate ring is further confirmed by the shift of the absorption band assigned to $\nu_{as}C=C=C$ from 1550 cm^{-1} (ligand) to 1529 cm^{-1} (Ca and Cd) and 1516 cm^{-1} (Sn). The vibrational frequency mode of interest in the 600-200 cm^{-1} region of IR are those due to metal - ligand and chelate ring vibrations. Hence, the unique bands in the IR spectra of metal complexes appearing at 416 cm^{-1} (Ca), 433 cm^{-1} (Cd), and 530 cm^{-1} (Sn); and absent in the IR spectrum of the ligand, have been assigned to νM-O of the metal complexes. The M-O and the chelate ring vibration frequency modes follow the order: Ca<Cd<Sn, which is the order of decreasing atomic weights of the metals.

NMR spectra. The ^{1}H and ^{13}C NMR assignments listed inTable 4 and 5 are made by comparison with published reports on NMR spectral properties on 4-acyl-oxo-pyrazoles and their metal complexes [1,6,7,9]. The ^{1}H NMR spectrum of HNP and the metal complexes in acetone-d_6 reveal a signal between 2.08 and 2.45 ppm for HNP and each of the metal complexes integrated for three protons and attributable to methyl group and followed by a multiplet between 8.25 and 8.45 ppm for the ligand and each of the metal complexes integrated for ten protons and assigned to two phenyl groups. The weak signals appearing in 3.90 and 3.96 ppm region of the metal complexes, which is absent in the spectrum of HNP are attributable to water protons [6, 7, 9], and confirms that the metal complexes are hydrated species.

The ^{13}C NMR spectral data of HNP and metal complexes are given in Table 5. The appearance of resonance signal for C(1) and C(3) to C(5) carbon atoms of the metal complexes downfield relative to that of HNP is probably due to the involvement of these atoms in the chelation process through electron delocalization as depicted in Figure 2. Thus, the chemical shifts observed in the Ca(II), Cd(II), and Sn(IV) complexes reaffirms the opinion that coordination occurred through the carbonyl oxygen atoms since only the C(4) and C(5), together with nearby protons gave appreciable chemical shifts [6, 9].

Table 4. ^{1}H NMR chemical shifts (δ) of HNP and Ca(II), Cd(II) and Sn(IV) Complexes in acetone-d_6.

Proton No.	1	6 and 10	7 -9	14	Water proton
HNP	2.43(s)	8.25 - 8.39(m)		1.15(d)	
Ca - NP	2.10(s)	8.28 - 8.41(m)	7.32 - 8.08	1.15(d)	3.90(s)
Cd - NP	2.08(d)	8.25 - 8.40(m)	7.32 - 8.15(m)	1.12(d)	-
Sn - NP	2.10(d)	8.27 - 8.47(m)	7.82 - 8.04(m)	1.3(s)	3.96(s)

s, singlet; d, doublet; m,multiplet.

Table 5. ^{13}C NMR chemical shift (δ) of HNP and Ca(II), Cd(II) and Sn (IV) complexes in acetone-d_6.

Carbon No.	1	2	3	4	5	6	7	8	9	10	11
HNP		149.10	204.24		163.85	122.25	129.61	123.75	129.11	122.25	134.74
Ca - NP	17.00	141.50	204.24	119.75	159.50	122.55	129.85	123.77	129.85	122.55	133.50
Cd - NP	14.00	149.80	204.24	119.15	163.47	125.65	129.80	125.65	129.80	122.48	134.94
Sn - NP	14.00	158.2	204.24	119.79	163.91	125.72	129.87	123.72	129.87	122.59	134.74

CONCLUSION

The bonds between HNP and a metal ion are formulated as σ bonds through the carbonyl and hydroxyl groups of the keto-enol form of the ligand, the hydroxyl proton being liberated during complexation. An electron pair from the oxygen atom of the carbonyl group of the ligand is donated to the metal ion to form a C=O-M bond.

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