Synthesis and Spectro Scopic Investigations of Mn (II), Co (II) and Ni (II) with 2- a Pyrrolyl-2-Ketoethanal Phenyl Hydrazone

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Abstract

In this communication the author reports the synthesis of a hydrazine of substituted pyrrole (PKPH), Its complexing behavior towards bivalent Mn (II), Co (II) and Ni (II) and their characterization by I.R. Spectra, electronic spectra and their magnetic moments to establish their octahedral structures.

Introduction

From a survey of the literature it is concluded that a number of coordination compounds with N, O and S as coordinating centers have been prepared under different conditions. Relatively less attention has been paid to the synthesis of hydra zones of substituted heterocyclic analogs of cyclopentadiene and their transition metal complexes. The author reports the synthesis of a hydrazine of substituted pyrrole
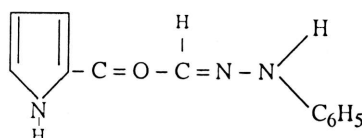
Fig. 1. Structure of the ligand PKPH (HL)

(PKPH), Fig. 1, its complexing behavior towards Mn (II), Co (II), Ni (II), and some thermodynamic parameters of these complexes.

Experimental

All reagents used were of A.R. grade. Elemental analyses were made by the microanalytical techniques. IR spectra were recorded on a Perkin Elmer-577 grating spectrophotometer using KBr pellets at room temperature. Electronic spectra were recorded on a Bausch and Lomb Spectronic-20 spectrophotometer and magnetic measurements were carried out at room temperature using the Guoy method pH-metric titrations were conducted on a Cambridge pH-meter in an inert atmosphere of nitrogen.

Preparation of the Ligand

Preparation of the ligand involves the following steps.

a. Preparation of 2-Acetylpyrrole. Since the acetylation of pyrrole (64) is typical, a unique method was employed. A mixture of phosphorus oxychloride (18 ml., 0.19 mole) and dimethylacetamide (10 mL., 0.103 moles) was kept for about 15-20 minutes at 10-20°C and then 25 mL (0.29 mile) of 1,2-dichloromethane was added to this mixture. The contents were cooled to 5°C in an ice-water bath and then were added slowly to 7.0 mL (0.08 mile) of pyrrole in 25 mL of 1.2-dichloroethane over a period of one hour. The reaction mixture was refluxed for about 20 minutes and then cooled to room temperature. To this liquid mass about 100 mL of a saturated solution of sodium carbonate was added and shaken vigorously. Two distinct layers form. The aqueous layer was extracted with 100 mL ether. The combined organic layers were washed with distilled water and dried when a crystalline mass was obtained. This was recrystallized from petroleum ether when given white needles of 2-acetylpyrrole, m.p. 92°C; yield 5.92 g (68%). Calculated % for C_6H_7NO : C 66.05; H 6.42; N 12.80. Found: C 66.40 H 6.60; N 12.60.

b. Oxidation of 2-Acetylpyrrole to the corresponding Glyoxal. 23.1 g (0.21 mile) of 2-acctylpyrrole in 200 mL. of dioxane were added to 24.4. g (0.22 mile) in a 500 mL round-bottomed flask fitted with a condenser. The contents were refuxed for 7.8 hours. A yellowish-orange liquid was obtained after distillation b.p. 105°C, yield 19.30 (~70%), Calculated % for v_1 $C_6H_5NO_2$ (F.W. 123); C. 58.53, H, 4.08; N. 11.43.

c. Preparation of 2-α Pyrrolyl-2-ketoethanalphenylhydrazone (PKPH)

In a 500 mL round-bottomed flask, suspend 5.40g. (0.05 mile) of phenylhydrazone in 50 mL of methanol and add about 5mL of 2 N H_2SO_4 cautiously. Filter the warm solution. To it, a solution of glyoxal of 2-acetylpyrrole 6.0 g. (0.05 mile) in 40mL of ether is added. Keep the contents for 15-20 minutes. A dark-brown solid mass makes its appearance which was collected by suction, filtered and washed with a little methanol. The derivative was recrystallized from dilute alcohol and dried, at m.p. 160°C. calculated % for $C_{12}H_{11}ON_3$: C,67.60; H,5.16; N,19.71 found C,67.93; H,5.15; N,19.79. .

Preparation of the Complexes

Mn (II) complex. A quantity of 1.97 g. (0.01 mile) of manganese chloride tetrahydrate in 35 mL of ethanol was added to 2.13 (0.01 mile) of the ligand in 40 mL of ethanol. The reaction mixture was digested in a water bath for about 10 minutes. After cooling the contents, a light-pink precipitate was obtained. It was filtered, washed with water followed by alcohol and dried in an oven at 60°C, m.p. 180°C.

Co (II) complex. 2.13 g. (0.01 mile) of the ligand in 35 mL of ethanol was added to a solution of 2.30 (0.01 mile) of cobalt chloride hexahydrate in 45 mL of ethanol. The contents were refluxed on a water bath for about 15 minutes. The reaction mixture was poured over ice when a brick-red colored precipitate was obtained. It was filtered, washed with ether and dried in an oven at 70°C m.p. 195°C.

Ni (II) complex. To a solution of 2.13 g. (0.01 mile) of the ligand in 40 mL of ethanol, a solution of 2.30g. (0.01 mile) of nickel chloride hexahydrate in 30 mL of ethanol was added with constant stirring. The reaction mixture was heated and on cooling, a red-coloured solid mass was obtained. It was washed with hot water and then diluted with alcohol. The fine crystals were dried in an oven at 100°C, m.p. 225°C.

Results and Discussion

2-α pyrrolyl-2-ketoethanalphenylhydrazone (PKPH) forms coloured complexes with Mn (II), Co (II), Ni(II) according to following equations.

$$PKPH + MX_2 + 2H_2O \rightarrow [M(PKPH)X.2H_2O] + HX \quad \text{where} \quad M = Mn(II), Co(II) \quad \text{and}$$
NI(II)

The stoichiometry, color and melting points of the metal complexes are given in Table 1. All the complexes are stable at room temperature and have an octahedral environment around each metallic ion.

Table–1: Analytical Data, Colour and Melting Points of 2-α Pyrrolyl-2-Ketoethanalphenylhydrazone

Complexes	Formula Weight	Color	M.P.C°	% M Caled. (Obsd)	% C Calcd. (Obsd)	% N Calcd. (Obsd)	% Cl Calcd. (Obsd)
$[Mn(C_{12}H_{10}N_3O)Cl.2H_2O]$	338.4	Light pink	180	16.22 (16.30)	42.55 (42.34)	12.41 (12.47)	10.49 (10.54)
$[Co(C_{12}H_{10}N_3O)Cl.2H_2O]$	342.4	Brick red	195	17.20 (42.26)	42.05 (42.26)	12.26 (12.20)	10.36 (10.41)
$[Ni(C_{12}H_{10}N_3O)Cl.2H_2O]$	342.2	Red	225	17.15 (17.23)	42.08 (42.20)	12.27 (12.33)	10.37 (10.38)

IR Spectra

The IR spectrum of the ligand (PKPH) in KBr shows sharp bands at $3420 \, cm^{-1}$, $1680 \, cm^{-1}$ and $1470 \, cm^{-1}$ which are assignable to $v(N-H), > C = 0$ and $v(C = N)$ vibrational modes, respectively. Some other bands of varying intensities have also appeared in the regions $1350 - 1650 \, cm^{-1}$ and $700 - 870 \, cm^{-1}$ which are assignable to characteristic skeletal and $\delta(C-H)$ or $\beta-$ ring vibrational modes. A comparison of the IR spectra of the free ligand and its metal complexes reveals an appreciable shift to lower wave numbers in the $> C = O$ and $-CH = N$ frequencies from and in the ligand to and in the complexes, respectively. This shift suggests the participation of the carbonyl oxygen and the azomethine nitrogen in the coordination of the ligand with the metal ions. Simultaneously, the disappearance of the band at on coordination, indicates the deprotonation and the involvement of the pyrrole () in the complexation. Participation of the pyrrole nitrogen () in the complexation has already been suggested by other workers earlier (1-2) and hence the ligand behaves as a tridentate.

A comparison of far IR spectra of all the complexes with those of the free ligand reveals two new bands in the and range which are tentatively assigned to M-O and M-N stretching vibrations, respectively. In all the metal complexes a band in the range also makes its appearance which has been assigned to the stretching frequency. Also, in all the complexes a new band at has been assigned to coordinated water molecule (3-5). Nakagawa and Shimanouchi (5) carried out normal coordinate analyses on (symmetry) and (symmetry) type ions to assign these low-frequency modes.

Electronic Spectra

Mn (II) Complex. At lower temperatures due to the sharpness of bands, a very accurate measurements may be made of electronic transition energies with d^5 complexes. The Mn (II) ion belongs to a d^5 system whose ground term is high spin complexes in ^6S. Since the ^6S term is orbitally non-degenerate, therefore, all the crystal field transitions from the term are orbitally non-degenerate, therefore, all the crystal field transitions from ^6S the term will be spin forbidden as well as Laporte forbidden. The crystal field spectra of high spin d^5 complexes are therefore, expected to be very weak. With the ground state $(t_{2g})^3$, $(e_g)^2$ the Mn(II) ion should have a magnetic moment value of 5.92 B.M. in an octahedral environment. The magnetic moment value of the present complex [Mn (PKPH)Cl.2H$_2$O], has been found to be 5.80 B.M. (Table 2), which is very close to the spin-only value of 5.92 B.M. for Mn (II) metal compounds.

The observed magnetic moment value suggests an octahedral environment of the ligand around the metal ion and the ground term of manganous ion in aqueous solutions is the sextet. The only sextet of d^5 configuration in an octahedral environment is $^6A_{1g}$, Consequently, there can be no spin-allowed transitions.

The intensities of octahedral Mn (II) complexes are extremely low as a consequence of their doubly forbidden nature. The electronic spectra of the present complex exhibit three bands at 17990, 20850 and 24550 cm^{-1} and these transitions have been assigned to $^6A_{1g} \rightarrow {}^4T_{2g}$, $^6A_{1g} \rightarrow {}^4A_{1g}$ (^4E) and $^6A_{1g} \rightarrow {}^4A_{1g}$ ^4E_g (G), respectively (Table II). The first transition, $^6A_{1g} \rightarrow {}^4A_{2g}$ possesses a low extinction coefficient, it is, therefore, probably a spin-forbidden band and the latter pair of transitions is degenerate in octahedral symmetry. By fitting the transition energy, $^6A_{1g} \rightarrow {}^4A_{1g}$. ^4E_g (G), and making use of the relationship Dq/B = 1.1, the values of B and Dq have been calculated and the value of β, calculated from the relation β = $\frac{B \text{ (in complex)}}{B \text{ (infreeion)}}$, suggests a partial covalent character of bonds in the present complex. It has been reported (6-7) that the interelectronic repulsion forces between d-electrons are decreased upon complexation. The decrease may be from 5% to 4% for the 3d series of metal complexes. The lowest values of are observed in tetrahedral complexes, especially those with more covalent ligands. β

Co (II) Complex. In high-spin complexes of Co (II) complexes the ground term is 4F and in low-spin complexes it is 2G. Although the colors of the metal compounds cannot be taken as infallible guides to their stereo chemistry, yet some clues may be drawn regarding the environment of the metal ion. As cited in the literature (8), most octahedral Co (II) derivatives are pink or reddish brown and most tetrahedral Co (II) derivatives are intense

blue or green. The present complex, [CO (PKPH) Cl.$2H_2O$], is brick-red, giving some clue of its octahedral geometry.

The magnetic moment value for the present complex is 4.62 B.M. (Table 2) which is less than the observed value (4.7-5.2 B.M.) for high-spin (sp^3d^2) octahedral Co (II) complexes. This may be attributed to incomplete quenching of the orbital contribution to the magnetic moments (9). The electronic configuration of cobalt is $3d^74s^2$, therefore, Co (II) ion would be $3d^7$ and must involve a weak ligand field with three unpaired electrons. The gaseous Co(II) ion has the ground state ^4F with the excited state ^4P which, under the influence of a cubic field, may split into $^4T_{2g}$ (F), $^4T_{1g}$ (F), $^4T_{2g}$ (F), $^4A_{2g}$ (F) and $^4T_{1g}$ (P), almost arranged in order of increasing energy. The $^4A_{2g}$ state is derived from Iron $(t_{2g})^3$ $(e_g)^4$ configurations and the $^4T_{1g}$ state from $(t_{2g})^5 (e_g)^2$ configuration. Therefore, it is evident that $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) is a two-electron transition. The electronic spectra of the present complex consist of four bands at 10510, 17050, 18990 and 20500 cm^{-1} which may be assigned to $^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F) (v_1), $^4T_{1g}$ (F) $\rightarrow$ $^2T_{1g}$. $^2T_{2g}$, $^4T_{1g}$ (F) $\rightarrow$ $^4A_{2g}$ (F) (v_2) and $^4T_{1g}$ (F) $\rightarrow$ $^4T_{1g}$ (P) (v_3) respectively.

Table 2: Electronic Spectra, Relevant Ligand Field Parameters and Magnetic Moments of Mn (II), Co (II), Ni (II) Complexes with 2 Pyrrolyl-2-keto ethanal phenyl hydrazine

Complexes	Transitions	Assignments cm^{-1}	Parameters cm^{-1}	μeff B.M.
[Mn(PKPH)Cl.$2H_2O$]	17990	$^6A_{1g} \rightarrow$ $^4T_{2g}$	Dq = 1055.0	5.80
	20850	$^6A_{1g} \rightarrow$ $^4A_{1g}$ (^4E)	B = 892.4	
	24550	$^6A_{1g} \rightarrow$ $^4A_{1g}$ ^4E_g(G)	β = 0.92	
[Co(PKPH)Cl.$2H_2O$]	10510	$^4T_{1g}$ (F) $\rightarrow$ $^4T_{2g}$ (F)(v_1)	10Dq = 1078.0	4.62
	17050	$^4T_{1g}$ (F) $\rightarrow$ $^2T_{1g}$. $^2T_{2g}$	B = 834.2	
	190090	$^4T_{1g}$ (F) $\rightarrow$ $^2A_{2g}$ (F)(v_2)	β = 0.85	
	20500	$^4T_{1g}$ (F) $\rightarrow$ $^2T_{2g}$ (P)(v_3)	$\dfrac{v_2}{v_1} = 1.80$	
			L.F.S.E. = 18.48 Kcal/Mole	
[Ni(PKPH)Cl.$2H_2O$]	87000	$^3A_{2g} \rightarrow$ $^3T_{2g}$ (F)(v_1)	10Dq = 8700.0	3.00
	(Obsd) 14255	$^3A_{2g} \rightarrow$ $^3T_{1g}$ (F)(v_2)	$\dfrac{v_2}{v_1} = 1.63$	
	(Calcd) 14300	$^3A_{2g} \rightarrow$ $^3T_{1g}$ (P)(v_3)	B = 810.02	

	(Obsd) 24000		$\beta = 0.77$	
	(Calcd) 23990		$\%C = 22.7$	
			L.F.S.E. = 24.8 Kcal/Mole	

The lowest and the highest energy bands may be assigned to v_1 and v_3 transitions and the shoulders may be considered either due to the splitting of v_3 in many components or by the appearance of a v_2 transition. To assign the shoulder as v_2 transition in the octahedral Co (II) Complex, Lever (10) suggested that the energy of this band should be approximately twice but not greater than 2.2 times that of the v_1 transition. For the present complex the ratio of $\frac{v_2}{v_1}$ is 1.81, which is in fair agreement with the reported values (1.97-2.07) and suggests that the shoulder must be at $17050 \, cm^{-1}$.

The nephelauxetic ratio arising out of the partial overlap of 3d orbitals with σ and π orbitals of the surrounding donors, consisting of both f_σ^2 and f_π^2 is 0.86. Because of this partial covalent character, there may be a decrease in the magnetic moment value. The existence of distortion from a regular octahedral structure is evidenced in Co (II) complexes by appreciable intensity enhancement.

Ni (II) Complex. The magnetic moments of Ni (II) complexes often vary with temperature and concentration. The magnetic moment at 300°K for the present complex [Ni(PKPH)Cl.2H$_2$O] is 3.0 B.M., a value well within a range reported for octahedral geometry (11). The spin-only value of nickel is 2.83 which is slightly lower, probably because of slight distortion from the pure octahedral to D_{4th} symmetry. Since, for a tetrahedral symmetry, which is capable of giving a triplet state as the ground state, the magnetic moments due to orbital contribution would have been more than the experimental value.

The d orbitals in an octahedral environment will split into two levels, the triply degenerate $t_{2g} (d_{xy}, d_{yz}$ and $d_{xy})$ and doubly degenerate $e_g (d_x{}^2 - y^2 . d_2{}^2)$ levels. Since the e_g orbitals point directly towards the ligands whilst the t_{2g} orbitals point between them, the energy order will be $e_g > t_{2g}$. The separation between the two sets Δ, is the measurement of 10 Dq and hence the energy levels may be used for d^8 configuration in an octahedral field (12).

The electronic spectra of the present complex consist of three different distinct bands at 8010-9060, 14000-15000 and 24500-25000 cm^{-1} which have been assigned to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)(v_1)$, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)(v_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)(v_3)$, respectively (Table II). The value of different parameters has been calculated by assuming octahedral symmetry around Ni (II) ion. The value of B, calculated by using the expression: $B = \frac{v_2 + v_3 - 3v_1}{15}$ indicates distortion from pure octahedral symmetry. For the spin-forbidden

transition $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ the energy values have been calculated by taking $^3A_{2g}(F) \rightarrow {}^1E_g(D)$ and these values differ from the values observed for Ni (II) complexes experimentally, supporting the distortion from the octahedral symmetry (13).

The present lowering of (P) relative to the Ni (II) free ion value of 15840 $_{cm^{-1}}$ was calculated to be 22.8. The value of L.F.S.E. was found to be 24.86 Kcal/Mole. All these values are in good agreement with the distorted octahedral geometry of the complex. By making use of the following equations:

$$E\left[{}^3A_{2g} \rightarrow {}^3T_{2g}(F)\right]; v_1 = \frac{15B}{2} + \frac{10Dq}{2} + \frac{1}{2}\left[(9B + 10Dq)^2 + 144B^2\right]^{1/2}$$

$$E\left[{}^3A_{2g} \rightarrow {}^3T_{1g}(F)\right]; v_2 = \frac{15B}{2} + \frac{3}{2}(10Dq) - \frac{1}{2}\left[(9B + 10Dq)^2 + 144B^2\right]^{1/2}$$

$$E\left[{}^3A_{2g} \rightarrow {}^3T_{1g}(P)\right]; v_3 = \frac{15B}{2} + \frac{3}{2}(10Dq) - \frac{1}{2}\left[(9B + 10Dq)^2 + 144B^2\right]^{1/2}$$

the theoretical values v_1, v_2 and v_3 have been calculated. Because the observed and the calculated values of v_2 and v_3 are close to each other, therefore, the cubic symmetry of the present complex is verified. From the above discussion we conclude that for the present Ni (II) complex to be octahedral, the following conditions must be fulfilled: (i) the value of B should be less than the free gaseous ion value, (ii) the experimental and the calculated values of v_2 and v_3 should in close agreement, and (iii) the ratio of v_2 / v_1 should be between 1.5 to 1.7. Based on the above observations and discussion an octahedral geometries of the Mn (II), Co (() and Ni (II) complexes are proposed.
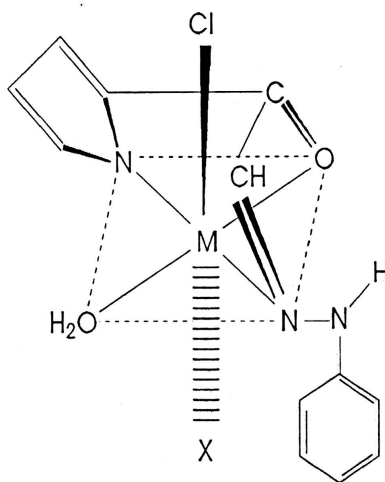
M = Mn(II), Co(II) and Ni(II) and X = H_2O

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