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Cobalt(II) and Zinc Complexes of 2-Acetyl- and 2-Benzoylpyridine Hydrazones

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Complexes derived from 2-acetylpyridine hydrazone (APH) and 2-benzoylpyridine hydrazone (BPH) have been prepared with cobalt(II) and zinc(II) salts. The mono-ligand complexes MX_2L (M = Co; X = Cl, Br; M = Zn; X = Cl; L = APH, BPH; M = Co; X = NCS; L = BPH) are tetrahedral while the bis-ligand complexes (M = Co; X = Cl, Br, NCS; L = APH, BPH; M = Zn; X = Cl; L = APH, BPH) contain octahedrally coordinated metal atoms. No tris-ligand complexes have been prepared. The ligands appear to coordinate via *both the pyridine and methylene nitrogen atoms.*

Introduction

Despite the interest in many ligands containing the –N=C–C=N– grouping *e.g.* dipyridyl, 1,10-phenanthroline and hydrazones of 1,2-diketones [1, 2], the coordination chemistry of hydrazones of 2-pyridyl ketones have received only scant attention. The ligand 2-pyridinal hydrazone gives six coordinate complexes $[M(PAH)_3]I_2$ (M = Fe, Co, Ni) resembling the dipyridyl analogues but, in con-

TABLE I. Complexes of APH and BPH with Cobalt(II) and Zinc Salts.

Complex	Colour	Elemental Analyses (%)[a]		
		C	H	N
$CoCl_2(APH)$	green	31.5(31.7)	3.58(3.40)	14.9(15.8)
$CoCl_2(APH)_2$	pale red	42.0(42.0)	4.16(4.53)	20.4(21.0)
$CoBr_2(APH)$	green	24.1(23.8)	2.60(2.56)	11.7(11.9)
$CoBr_2(APH)_2$	pale red	34.6(34.4)	3.92(3.71)	17.5(17.2)
$Co(NCS)_2(APH)$	dark red	34.4(34.8)	3.00(2.92)	21.8(22.5)
$Co(NCS)_2(APH)_2 \cdot H_2O$	orange	41.7(41.5)	3.74(4.35)	24.1(24.1)
$ZnCl_2(APH)$	yellow	30.8(31.0)	3.20(3.34)	15.3(15.5)
$ZnCl_2(APH)_2$	pale pink	41.4(41.4)	4.43(4.46)	20.6(20.7)
$CoCl_2(BPH)$	green	43.5(44.1)	3.71(3.39)	11.5(12.8)
$CoCl_2(BPH)_2 \cdot H_2O$	pale red	52.6(53.1)	4.22(4.46)	15.8(15.5)
$CoBr_2(BPH) \cdot 2H_2O$	green	32.6(31.9)	3.32(3.34)	9.02(9.29)
$CoBr_2(BPH)_2$	pale red	46.2(47.0)	3.58(3.61)	13.6(13.7)
$Co(NCS)_2(BPH)_2$	orange	54.7(54.8)	4.00(3.89)	19.7(19.7)
$Co(NCS)_2(BPH) \cdot H_2O$	green	43.0(43.1)	3.24(3.55)	16.8(17.9)
$ZnCl_2(BPH)$	yellow	42.7(43.2)	3.35(3.32)	12.2(12.6)
$ZnCl_2(BPH)_2 \cdot H_2O$	pale pink	52.9(52.5)	4.34(4.40)	15.3(15.3)

[a] Theoretical values in parentheses.

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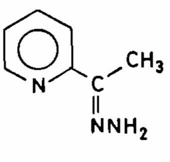
TABLE II. Physical Properties of APH and BPH Complexes.

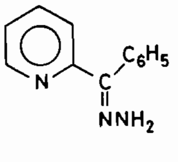
Complex	Magnetic Moment μ_{eff} (BM)	Electronic Spectra (10^3 cm^{-1})			Molar Conductivity[a] Λ_M (ohm^{-1} mol^{-1} cm^2)
		Solid State		Solution (ϵ in parentheses)	
Tetrahedral		$^4A_2 \rightarrow {}^4T_1(P)$	$^4A_2 \rightarrow {}^4T_1(F)$		
$CoCl_2(APH)$	4.7	16.6	8.7, 7.6, 6.0		insol
$CoBr_2(APH)$	4.8	16.4	8.6, 7.5, 6.4		insol
$CoCl_2(BPH)$	4.3	15.8, 15.1	7.6, 6.1, 5.1	15.8(280)	38.9
$CoBr_2(BPH)\cdot 2H_2O$	4.5	15.8, 15.0	7.2, 6.0, 5.1	16.1(310)	60.3
$Co(NCS)_2(BPH)\cdot H_2O$	4.8	15.9	8.6, 7.5, 6.6	16.2(330)	20.9
Octahedral		$^4T_{1g} \rightarrow {}^4A_{2g}, {}^4T_{1g}(P)$	$^4T_{1g} \rightarrow {}^4T_{2g}$		
$CoCl_2(APH)_2$	4.9	21.2, 19.1	9.4	20.6(62)	7.2
$CoBr_2(APH)_2$	4.9	20.6, 19.2	9.2		
$Co(NCS)_2(APH)_2\cdot H_2O$	4.8	20.2	10.2	21.0(155)	11.4
$CoCl_2(BPH)_2\cdot H_2O$	4.9	19.8	9.5	20.5(44)	3.0
$CoBr_2(BPH)_2$	5.0	19.4	9.3	20.1(148)	24.7
$Co(NCS)_2(BPH)_2$	4.8	19.8	10.7	21.0(144)	35.0
Unassigned					
$Co(NCS)_2(APH)$	4.7	18.6	9.1, 8.2		insol.
$ZnCl_2(APH)$	diamagnetic				20.6
$ZnCl_2(APH)_2$	diamagnetic				27.3
$ZnCl_2(BPH)$	diamagnetic				20.5
$ZnCl_2(BPH)_2\cdot H_2O$	diamagnetic				26.6

[a] 10^{-3} *M* solutions in CH_3NO_2.

trast to the reactions of hydrazone ligands, derived from diketones, no four coordinate complexes have been obtained with this ligand [3]. We here report the preparation and properties of complexes of cobalt(II) and zinc with the previously unstudied ligands 2-acetylpyridine hydrazone (APH) and 2-benzoylpyridine hydrazone (BPH)



APH



BPH

Results and Discussion

The new ligands APH and BPH were obtained as crystalline solids from the reactions between hydrazine and the respective pyridyl ketones. The complexes (Table I) were obtained by direct reaction of the metal salts with the ligands in ethanol. Unlike 2-pyridinal hydrazone [3] the ligands APH and BPH do not form tris-complexes with these metal ions even when the ligands are in excess. Instead we find 1:1 (M:L) and 1:2 complexes. The magnetic moments and electronic spectra of the 1:1 complexes (Table II) show these to have tetrahedral stereochemistry around the cobalt(II) ions. The $^4A_2 \rightarrow {}^4T_1(F)$ band in these complexes is split into three bands indicating reduction of symmetry from T_d to C_{2v}, the bands arising from transitions to the $^4B_1$, $^4A_2$ and $^4B_2$ states [4]. Those compounds which are soluble in nitromethane have the relatively high molar absorption coefficients expected for pseudo-tetrahedral complexes and have molar conductances which indicate very little ionisation (1:1 electrolytes have $\Lambda_M \sim 92$ ohm^{-1} mol^{-1} cm^2 on average [5]).

In contrast to the green 1:1 complexes, the orange-red 1:2 complexes (Table I) have magnetic moments and electronic spectra (Table II) typical of pseudo-octahedral complexes; the broad band around 20,000 cm^{-1} being usually unresolved into the $^4A_{2g}$

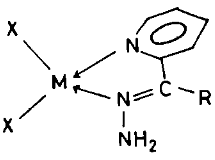
TABLE III. Important Infrared Bands (cm^{-1}) in APH, BPH and their Complexes.

Compounds	ν(CN)$_{NCS}$	ν(C=N$_2$)	ν(N–N)	ν(CS)	δ(NCS)	ν(MX)	ν(MN$_2$)
APH		1579	1149				
BPH		1560	1149				
$CoCl_2$(APH)		1597	1177			282	269
$CoBr_2$(APH)		1597	1172			240	270
$CoCl_2(APH)_2$		1590	1161			225	267
$CoBr_2(APH)_2$		1591	1158				269
$Co(NCS)_2$(APH)	2058	1580	1161	811	479		278
$Co(NCS)_2(APH)_2 \cdot H_2O$	2058	1591	1160	791	475		262
$ZnCl_2$(APH)		1600	1165			342, 296	265
$ZnCl_2(APH)_2$		1593	1160			255	265
$CoCl_2$(BPH)		1595	1158			290br	
$CoBr_2$(BPH)		1595	1158			238	
$CoCl_2(BPH)_2 \cdot H_2O$	2048	1589	1154			256	
$CoBr_2(BPH)_2$		1590	1152				
$Co(NCS)_2(BPH) \cdot H_2O$	2048	1589	1155	obsc	475		
$Co(NCS)_2(BPH)_2$	2062	1584	1150	obsc	471		254
$ZnCl_2$(BPH)		1592	1158			295br	
$ZnCl_2(BPH)_2 \cdot H_2O$		1594	1159			269br	255

and $^4T_{1g}$(P) components. In nitromethane solution the complexes are non-electrolytes and while the molar absorption coefficients of the band around 20,000 cm^{-1} are larger than is usual for octahedral complexes, the band position confirms that no dissociation into the tetrahedral complex plus free ligand has occurred. There is a charge-transfer band in the spectra of the complexes around 28,000 cm^{-1} and the relatively large values of ϵ for the 20,000 cm^{-1} band in the octahedral complexes probably arise from intensity stealing from the higher energy band.

The IR spectra of the metal halide complexes support the structural assignments. Thus the mono-ligand complexes of the metal chlorides and bromides show ν(M–X) in the region expected [6] for tetrahedral complexes while the bis-ligand complexes show ν(M–Cl) below 260 cm^{-1} and no ν(M–Br) which is expected to lie below 200 cm^{-1}. The IR spectra of the ligands show the ν(CN) bands at 1579 cm^{-1} (APH) and 1560 cm^{-1} (BPH); an increase of ν(CN) occurs when the ligands co-ordinate, which is indicative of coordination of the ligand through the nitrogen atoms of the C=N bonds. Similar increases of ν(CN) are observed when acetonitrile [7] and glyoxalbisdimethylhydrazone [1] undergo coordination to a metal. We assign the strong band at 1149 cm^{-1} in the ligands to ν(NN); such an assignment is in accord with the established ν(NN) in hydrazine (1098 cm^{-1}) [8] and the assigned ν(NN) in glyoxalbisdimethylhydrazone (1132 cm^{-1}) [1] and formaldehydedimethylhydrazone (1137 cm^{-1}) [9]. In the complexes there is a small shift (Table III) of ν(NN) to higher wavenumbers; similar shifts are observed in hydrazine complexes [8] and this is again indicative of coordination from one of the nitrogen atoms of the N–N bond. Evidence for the non-bonding of the NH_2 nitrogen atom comes from the N–H stretching region. In APH, the N–H stretching frequencies occur at 3358, 3298 and 3182 cm^{-1} while in BPH they occur at 3355, 3281 and 3190 cm^{-1}. The complexes of APH show N–H stretching frequencies in the regions 3378–3340, 3300–3238 and 3200–3140 cm^{-1} while BPH complexes show them in the regions 3398–3342, 3280–3255 and 3180–3160 cm^{-1}. Some reduction in ν(NH) is expected to arise from hydrogen bonding of the NH protons with the bonded anions so that any reductions in (NH) observed are not as large as expected if coordination of the NH_2 nitrogen atom had occurred. On the other hand there is evidence that the pyridine nitrogen atom is coordinated to the metal in these complexes. The ring deformation bands in the ligands are at 401 (out-of-plane) and 620 cm^{-1} (in-plane); in the complexes, these bands shift to higher frequencies and are typically at 420 and 640 cm^{-1}. Similar shifts have been recorded for pyridine complexes with metal halides [10]. We thus believe these ligands to coordinate *via* the methylene and pyridine nitrogen atoms and thus to belong to the class of chelating ligands containing the –N=C–C=N– grouping. The tetrahedral cobalt-

(II) complexes (Table II) and the zinc complexes $ZnCl_2(APH)$ and $ZnCl_2(BPH)$ are thus believed to have the structure:



The octahedral complexes are almost certainly neutral bis chelates; it is surprising that cationic tris chelates are not formed. All the thiocyanate complexes show ν(CN) close to the free ion value (2053 cm^{-1} in KNCS) indicating that the thiocyanate ions are N-bonded and terminal [11] (bridging thiocyanate exhibits ν(CN) above 2100 cm^{-1}). Similarly, the positions of the NCS deformation mode and the CS stretching mode are indicative of N-bonded thiocyanates. The dark red complex $Co(NCS)_2(APH)$ is curiously different to the green compounds CoX_2-(APH) and $Co(NCS)_2(BPH)\cdot H_2O$ and its spectral and magnetic properties cannot be assigned to either tetrahedral or octahedral stereochemistry.

Experimental

Electronic spectra were measured on a Unicam SP700C instrument and infrared spectra on a Perkin-Elmer 577 spectrophotometer using caesium iodide plates. Magnetic moments were obtained by the Gouy method at room temperature. Hydrated cobalt-(II) halides were dehydrated at 100 °C *in vacuo*.

Preparation of Ligands

The hydrazones were prepared by direct reaction between 2-acetyl- and 2-benzoyl-pyridine (ex Aldrich) and a slight excess of hydrazine hydrate in ethanol. After heating under reflux for 24 h, the solutions were concentrated by removal of ethanol *in vacuo* until cooling in the refrigerator caused crystallisation. The white crystals were filtered off, washed with cold (0 °C) ethanol and recrystallised from hot ethanol before being finally washed with ether and dried *in vacuo*. *Anal.* Found: 2-acetylpyridine hydrazone, m.p. 69–70 °C; C, 62.9; H, 6.25; N, 30.8; $C_7H_9N_3$ requires C, 62.2; H, 6.71; N, 31.1%: 2-benzoylpyridine hydrazone, m.p. 99–100 °C; C, 72.8; H, 5.52; N, 21.2; $C_{12}H_{11}N_3$ requires C, 73.1; H, 5.62; N, 21.3%.

Preparation of Complexes

The anhydrous (hemi-hydrate in the case of $Co(NCS)_2$) metal salt was heated under reflux in ethanol for 1 h with less than the stoichiometric quantity of the hydrazone (typically MX_2:ligand used was 1.4:1) for the 1:1 complexes and more than the stoichiometric quantity (typically MX_2:ligand = 1:2.2) for the 1:2 complexes. All the cobalt(II) complexes were prepared under an atmosphere of nitrogen. The complexes of APH were frequently deposited during the reflux and crystallisation was completed by cooling the mixtures in the refrigerator. With the exception of the $Co(NCS)_2$ complexes, complexes of BPH did not crystallise from ethanol but were precipitated by the addition of small quantities of ether to the cooled solutions. All the complexes were washed with ether and dried *in vacuo*.

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