

Hydrazone Ligands Derived from Acyl- and Aroyl-ferrocenes and their Complexes with Cobalt(II) Halides

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Current interest in the coordination chemistry of hydrazones has arisen through their uses in for example biological systems [1] and analytical chemistry [2]. Our own work [3–5] has so far concentrated on hydrazones containing the $-N=C-N-$ chelating linkage, these hydrazones form very stable compounds with metal ions in the first transition series. No coordination chemistry of a hydrazone which already contains a metal atom has been studied. In this paper we report the extension of our work to a study of the donor properties of the hydrazones of formylferrocene (FFH), acetylferrocene (AFH), benzoylferrocene (BFH) and the dimethylhydrazones of formylferrocene (FFDMH) and acetylferrocene (AFDMH).

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Experimental

Experimental techniques were as described previously [3]. Cobalt(II) halides were dehydrated at 100 °C *in vacuo*. The hydrazones were prepared from the carbonyl compounds and anhydrous or aqueous hydrazines in ethanolic solution. The preparation of acetylferrocene hydrazone is typical. Acetylferrocene (4.9 g; 0.022 mol) was dissolved in absolute ethanol (25 cm³) and treated with anhydrous hydrazine (4.0 cm³; 0.12 mol). The mixture was heated under reflux for 24 h and the hot mixture then filtered, reduced in volume to one-half and the yellow hydrazone precipitated by the addition of water (50 cm³). The product was filtered off, dried *in vacuo* and purified using an alumina column. Any unreacted ketone was eluted with dichloroethane and the hydrazone was eluted with ethyl acetate. Elemental analyses of the hydrazones are presented in Table I and principal features of their IR spectra in Table II. We were unable to isolate the dimethylhydrazone of benzoylferrocene from the reaction between 1,1-dimethylhydrazine and benzoylferrocene even after heating the mixture under reflux in ethanol for 48 h.

Preparation of Complexes

Whilst being stable in the solid state, the ligands were found to be unstable in solution. Solutions of the hydrazone of acetylferrocene, for example, rapidly deposit iron metal at room temperature so that we initially had difficulty in isolating complexes free from metallic iron. The following method, exemplified by the preparation of $CoCl_2(AFH)_3$, worked well however.

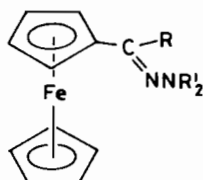
TABLE I. Hydrazone Ligands Derived from Formyl-, Acetyl- and Benzoyl-ferrocenes and their Complexes with Cobalt(II) Halides

	Colour	Elemental analysis, found (calc.) (%)			X (Cl or Br)	Λ_m^a (ohm ⁻¹ mol ⁻¹ cm ²)	μ_{eff} (BM) (20 °C)
		C	H	N			
AFH	orange	59.26 (59.60)	5.75 (5.78)	11.31 (11.57)			
$CoCl_2(AFH)_3$	pale pink	50.33 (50.46)	5.26 (4.90)	9.43 (9.81)	8.14 (8.29)	3.08	5.04
$CoBr_2(AFH)_3$	pink	45.52 (45.72)	4.44 (4.44)	8.45 (8.88)		2.78	5.14
AFDMH	orange	62.34 (62.22)	6.81 (6.66)	9.71 (10.37)			
$CoCl_2(AFDMH)_3$	pink	53.81 (53.60)	5.45 (5.70)	8.72 (8.90)	7.39 (7.55)	3.45	5.00
$CoBr_2(AFDMH)_3$	pink	49.12 (48.98)	5.17 (5.25)	8.04 (8.16)		2.78	5.10
BFH	orange	67.53 (67.10)	5.41 (5.26)	8.99 (9.21)			
$CoCl_2(BFH)_3$	brown	59.51 (58.73)	4.74 (4.60)	7.81 (8.06)		3.08	5.11
$CoBr_2(BFH)_3$	brown	53.86 (54.11)	4.27 (4.24)	7.31 (7.42)		3.45	5.14
FFH	orange	57.38 (57.89)	5.07 (5.26)	12.13 (12.28)			
$CoCl_2(FFH)_2$	pink	44.87 (45.05)	4.11 (4.09)	9.95 (9.55)		2.30	4.97
$CoBr_2(FFH)_2$	pink	39.26 (39.11)	3.99 (3.55)	8.67 (8.29)		2.13	5.03
FFDMH	orange	60.76 (60.94)	6.27 (6.25)	11.28 (10.94)			
$CoCl_2(FFDMH)_2$	pink	48.32 (48.60)	4.78 (4.98)	9.02 (8.72)		2.13	5.05
$CoBr_2(FFDMH)_2$	pink	42.36 (42.68)	4.64 (4.38)	7.92 (7.66)		1.83	5.12

^aValues of molar conductivity for 10⁻³ M solutions in CH₃NO₂ at 25 °C.

TABLE II. Principal Infrared Bands and Electronic Spectra of Hydrazones of Formyl-, Acetyl- and Benzoyl-ferrocenes and their Complexes with Cobalt(II) Halides

Compound	Principal IR bands (cm ⁻¹)			Electronic spectra (cm ⁻¹ × 10 ³)			
	$\nu_{as}(\text{NH}_2)$	$\nu_g(\text{NH}_2)$	$\delta_s(\text{NH}_2)$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	Solid state (reflectance)	Solution (ϵ in parentheses)
AFH	3410, 3388	3170, 3080	1634	1591	1145	22.4	
CoCl ₂ (AFH) ₃	3278, 3212	3090	1597	1575	1169	21.8, 9.0	22.1(39), 10.0(3)
CoBr ₂ (AFH) ₃	3252, 3210	3085	1595	1568	1170	22.2, 9.1	22.2(29), 9.9(2)
AFDMH				1596	1149	22.2	
CoCl ₂ (AFDMH) ₃				1590	1162	21.5, 15.4(sh)	22.1(25), 16.6(9), 14.6(5)
CoBr ₂ (AFDMH) ₃				1610	1168	21.8, 14.9, 13.8, 7.2	19.9(42), 16.1(11), 14.9(11), 14.3(12), 7.4(1)
BFH	3348, 3200	3081	1618	1560	1149	21.5	
CoCl ₂ (BFH) ₃	3280, 3212		1599	1569	1168	19.6, 14.5	21.6(22), 16.8(15), 15.7(12), 14.7(7.5)
CoBr ₂ (BFH) ₃	3242, 3199		1591	1559	1168	19.6, 14.5	20.0(28), 14.1(6)
FFH	3390	3099	1630	1576	1145	21.7	
CoCl ₂ (FFH) ₂	3282, 3218	3098	1630	1572	1168	21.7, 15.4(sh), 9.3	21.5(40) (other bands obscured)
CoBr ₂ (FFH) ₂	3262, 3210	3098	1629	1568	1172	21.2, 15.4(sh)	21.5(28) (other bands obscured)
FFDMH				1584	1139	22.2	
CoCl ₂ (FFDMH) ₂				1600	1170	22.4, 15.9, 15.0, 14.5, 8.0	21.5(4), 16.9(27), 15.6(17), 14.9(16.5), 8.1(4)
CoBr ₂ (FFDMH) ₂				1582	1165	21.0, 15.1, 14.4, 13.9, 7.6	19.5(25), 16.1(11), 14.9(7), 14.5(6), 8.0(1)



I; R = H, CH₃, R' = H, CH₃
R = C₆H₅, R' = H

Acetylferrocene hydrazone (1.21 g; 0.005 mol) was dissolved by heating in absolute ethanol (20 cm³) and the hot solution filtered into a solution of cobalt(II) chloride (0.162 g; 0.00125 mol) in hot absolute ethanol (15 cm³). The mixture was kept at the boiling point for 5 min and a pink precipitate formed; the mixture was cooled to room temperature, filtered and the precipitate washed with ethanol and ether before being dried *in vacuo*. Colours and analytical data on the complexes are given in Table I.

Results and Discussion

The addition-elimination reaction between acyl- and arylferrocenes and hydrazine or dimethylhydrazine yield the ligands I as orange crystalline solids.

Solutions of these ligands in ethanol decompose slowly; the relative order of stability being formyl > acetyl- > benzoyl-hydrazones with dimethylhydrazones being more stable than hydrazones. Complexes of these hydrazones with cobalt(II) chloride and bromide have been prepared in absolute ethanol and isolated as pink or brown microcrystals. Curiously the hydrazones of acetyl- and benzoyl-ferrocenes gave tris-complexes CoX₂L₃ (L = AFH, AFDMH or BFH; X = Cl, Br), while only bis-complexes could be obtained from hydrazones of formylferrocene (Table I) even though the ligand was present in excess. The complexes are soluble in nitromethane in which they give non-conducting solutions (Table I). Their magnetic moments are in the range 4.97–5.14 BM indicating a high orbital contribution to the magnetic moment of a high spin cobalt(II) (d⁷) system. They are thus magnetically dilute and there is evidently no magnetic interaction between the cobalt(II) ion and the diamagnetic iron(II) ion.

The electronic spectra of the complexes (Table II) show a weak band in the 7000–9000 cm⁻¹ region, a more intense band in the 15 000 cm⁻¹ region and a further band around 22 000 cm⁻¹. In some cases, e.g. the complexes of AFH and the solution spectra of FFH complexes, the broad band centred around 22 000 cm⁻¹ tails across the visible and obscures the bands around 15 000 cm⁻¹. The molar absorption coefficients (Table II) clearly show these bands to arise from d-d transitions. Further they are in the region expected from six coordinate cobalt(II). We

assign the band at $22\,000\text{ cm}^{-1}$ however, to the ${}^1A_{1g} \rightarrow {}^1E_{1g}$ transition in the iron atom of the cyclopentadienyl ligand; its position in the complexes is often close to that in the free ligand and is also close to and of the same intensity as that in ferrocene itself [6]. The two lower energy bands are in positions typically found for tetragonal cobalt(II) complexes; the lowest energy band being assigned to the ${}^4T_{1g} \rightarrow {}^4B_{2g}, {}^4E_g$ transition and the $15\,000\text{ cm}^{-1}$ band to the ${}^4T_{1g} \rightarrow {}^4B_{1g}$ transition. Our spectra resemble those found for other tetragonal systems of cobalt(II) [7]. The transitions to the 4E_g and ${}^4A_{2g}$ components (of ${}^4T_{1g}(P)$ in O_h symmetry) are expected to occur in the $19\,000\text{--}23\,000\text{ cm}^{-1}$ region and are almost certainly obscured by the more intense bands from the ligands in this region. Five coordination in the CoX_2L_3 type complexes is unlikely because of the low values of the molar absorption coefficients (high spin trigonal bipyramidal complexes of cobalt(II) have $\epsilon \sim 50\text{--}500\text{ l mol}^{-1}\text{ cm}^{-1}$ in the visible region [6]) and the absence of bands in the $11\,000\text{--}13\,000\text{ cm}^{-1}$ region. Further, $\nu(\text{Co}\text{--}\text{Cl})$ should appear above 200 cm^{-1} in the IR spectrum for a five coordinate complex.

The principal IR bands for the ligands and the complexes are shown in Table II. We assign the strong band in the $1100\text{--}1200\text{ cm}^{-1}$ region to $\nu(\text{N}\text{--}\text{N})$ in accord with the assignment of this mode in N_2H_4 at 1098 cm^{-1} [8]. The shift of this band to higher wavenumbers in going from the free ligand to the complexes is typical of coordination from the nitrogen atoms; in N–N bonded ligands which are bonded to a metal through the imino nitrogen only, an upward shift for $\nu(\text{N}\text{--}\text{N})$ of around 30 cm^{-1} is typical [5, 9] while in complexes containing bridging N–N ligands, an upward shift of $50\text{--}80\text{ cm}^{-1}$ is usually observed [8]. Our spectra therefore support bonding by unidentate hydrazones; the shift of $\nu_{\text{as}}(\text{NH}_2)$ and $\nu(\text{C}=\text{N})$ to lower wavenumbers are indicative of the

fact that it is the terminal amino nitrogen atom (N^2) which is coordinating in our complexes. This nitrogen atom is especially prone to being the coordination site when it has two methyl groups attached, as in the dimethylhydrazone complexes, which further increase its basicity [10].

The absence of cobalt–chlorine stretching frequencies above 200 cm^{-1} is indicative of a bridging chloride structure. We therefore conclude that the complexes have a polymeric doubly halogen-bridged six coordinate structure with terminal hydrazone ligands. In the tris-ligand complexes an extra molecule of ligand appears to be encapsulated within the structure but we are unable to detect this uncoordinated ligand spectroscopically. The fact that this third molecule of ligand is not present in the formylhydrazones suggests that steric factors may be important.

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