

Co-ordination Compounds Derived from Dimethylhydrazones of Cyclohexane-1,2-dione, 2-Acetyl- and 2-Benzoylpyridines and 4-Benzoylpyridine

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The 1,1-dimethylhydrazones of cyclohexane-1,2-dione (CDDMH), 2-acetylpyridine (APDMH) and 2-benzoylpyridine (2BPDMH) form tetrahedral complexes MX_2L ($M = Co(II), Zn(II)$; $X = Cl, Br$) in which the ligand is chelating through the methylene nitrogen atoms (CDDMH) or one methylene and one pyridine nitrogen atom (APDMH, 2BPDMH). Octahedral complexes CoX_2L_2 ($X = Cl, NCS$; $L = APDMH, 2BPDMH$) have also been isolated but no tris-ligand complexes. The ligand 4-benzoylpyridine-dimethylhydrazone (4BPDMH) does not chelate but forms tetrahedral complexes $MX_2(4BPDMH)_2$ in which the unidentate ligand co-ordinates through the pyridine nitrogen atom.

Introduction

Ligands containing the $-N=C-C=N-$ grouping are amongst the best known chelating agents e.g. 2,2'-dipyridyl and 1,10-phenanthroline. Because they fall into this class, we are currently studying the ligands formed by condensation of hydrazines with 1,2-diketones. Stoufer and Busch [1] were the first to prepare complexes of diacetyl dihydrazone; more recently, Ray and Sahoo [2] have shown that the complexes of formula $M(DADH)_2X_2$ ($DADH =$ diacetyldihydrazone; $M = Ni, Co$; $X = Br, I, SCN, NO_3, BF_4$) have a nearly octahedral arrangement of ligand atoms around the metal atoms. The dimethylhydrazone of diacetyl has been studied as a ligand only recently however. The copper(I) chloride complex $CuCl(DADMH)$ [3] and several metal carbonyl-DADMH complexes [4–6] have been characterised by tom Dieck and co-workers. A crystal structure determination of $Ni(CO)_2(DADMH)$ [7] has shown

that the ligand acts in a chelating fashion bonding through the methylene nitrogen atoms to the nickel to complete a tetrahedral environment. Recently we have shown [8] that tetrahedral complexes of the type $MX_2(DADMH)$ ($M = Fe, Co, Ni, Cu, Zn$; $X = Cl, Br, NCS$) also contain the chelating ligand and that unlike DADH, DADMH does not form six co-ordinate complexes even with metals for which the tetrahedral stereochemistry is rare e.g. Ni(II).

The hydrazones of acyl- or aroyl-pyridines occupy an intermediate position between the dipyridyl type ligands and the dihydrazones of α -diketones. We have recently shown however [10] that unlike 2,2'-dipyridyl and diacetylhydrazone, the hydrazones of 2-acetyl- and 2-benzoylpyridine are capable of forming both tetrahedral and octahedral complexes with cobalt(II) and zinc(II).

We report here on the complexes formed by the dimethylhydrazones of cyclohexane-1,2-dione (CDDMH), 2-acetylpyridine (APDMH), 2-benzoylpyridine (2BPDMH) and 4-benzoylpyridine (4BPDMH).

Results and Discussion

The new ligands studied in this work are not readily isolable in a pure form (being oils) and the complexes (Table I) were usually therefore prepared by the template synthesis (see Experimental) using ethanolic solutions of the metal salt, the carbonyl compound and 1,1-dimethylhydrazine. All four ligands form tetrahedral complexes with cobalt(II) chloride and cobalt(II) bromide. The magnetic moments and electronic spectra (Table II) of the complexes CoX_2L ($L = CDDMH, APDMH$ and $2BPDMH$) clearly show them to be tetrahedral both in the solid state and in nitromethane solution. These complexes are also un-ionised in nitromethane and the ligands are therefore bidentate. The dia-

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TABLE I. Complexes of Cyclohexanedione Dimethylhydrazone (CDDMH) 2-Acetylpyridine Dimethylhydrazone (APDMH) and 2-Benzoylpyridine Dimethylhydrazone (2BPDMH) and 4-Benzoylpyridine Dimethylhydrazone (4BPDMH).

Complex	Colour	Elemental Analyses (%)		
		C	H	N
CoCl ₂ (CDDMH)	green	37.0(36.8)	5.98(6.18)	17.5(17.2)
CoBr ₂ (CDDMH)	green	29.5(28.9)	5.05(4.86)	13.4(13.5)
ZnCl ₂ (CDDMH)	yellow	36.7(36.1)	6.21(6.06)	15.0(16.8)
CoCl ₂ (APDMH)	green	37.3(36.9)	3.76(4.47)	14.2(14.3)
CoBr ₂ (APDMH)	green	28.7(28.3)	3.50(3.43)	11.2(11.0)
ZnCl ₂ (APDMH)	yellow	36.4(36.1)	4.39(4.38)	13.9(14.0)
CoCl ₂ (APDMH) ₂ ·H ₂ O	red	45.6(45.6)	5.73(5.95)	17.1(17.7)
Co(NCS) ₂ (APDMH) ₂	red	47.7(47.9)	5.05(5.22)	21.3(22.3)
CoCl ₂ (2BPDMH)	green	46.6(47.3)	4.36(4.26)	11.6(11.8)
CoBr ₂ (2BPDMH)	green	37.9(37.9)	3.51(3.41)	9.13(9.46)
ZnCl ₂ (2BPDMH)	yellow	46.1(46.5)	4.34(4.18)	12.0(11.6)
CoCl ₂ (2BPDMH) ₂ ·3H ₂ O	red	52.5(52.9)	5.40(5.67)	12.6(13.2)
Co(NCS) ₂ (2BPDMH) ₂ ·3H ₂ O	red	49.6(49.5)	4.27(5.29)	15.6(16.4)
CoCl ₂ (4BPDMH) ₂	green	58.2(57.3)	5.17(5.15)	14.5(14.3)
CoBr ₂ (4BPDMH) ₂	green	50.5(50.3)	4.60(4.52)	12.4(12.6)
ZnCl ₂ (4BPDMH) ₂	yellow	57.8(57.9)	5.19(5.21)	14.3(14.5)

TABLE II. Physical Properties of Complexes of CDDMH, APDMH, 2BPDMH and 4BPDMH.

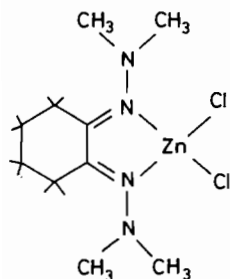
Complex	Magnetic Moment μ_{eff} (BM)	Electronic Spectra (10^3 cm^{-1})				Molar Conductivity ^a Λ_{M} ($\text{ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$)
		Solid State		Solution ^a (ϵ in parenthesis)		
<i>Tetrahedral</i>		${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{P})$ ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1(\text{F})$				
CoCl ₂ (CDDMH)	4.62		7.4	14.5(305)	7.0(110)	4.0
CoBr ₂ (CDDMH)	4.74	14.2	7.2	14.5(390)	7.0(119)	6.9
CoCl ₂ (APDMH)	4.76	15.5	7.0	15.0(341)	7.5(50)	4.4
CoBr ₂ (APDMH)	4.67	15.0	7.4	15.2(590)	7.2(55)	5.9
CoCl ₂ (2BPDMH)	4.85	16.6	9.0, 6.0, 5.5	14.8(390)	7.4(58)	9.0
CoBr ₂ (2BPDMH)	4.79	14.9	7.3, 6.8	15.0(341)	7.3(63)	9.5
CoCl ₂ (4BPDMH) ₂	4.78	15.9	9.1, 7.5, 6.3	15.0(850)	6.9(83)	9.0
CoBr ₂ (4BPDMH) ₂	4.72	15.3	9.0, 7.5, 6.4	15.2(1150)	7.0(110)	9.6
<i>Octahedral</i>		${}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{T}_{1\text{g}} \rightarrow {}^4\text{A}_{2\text{g}} \rightarrow {}^4\text{T}_{2\text{g}}$				
CoCl ₂ (APDMH) ₂ ·H ₂ O	4.93	24.5	19.2	9.6	15.1(520)	45.2
Co(NCS) ₂ (APDMH) ₂	4.97	22.0	19.4	9.0	^b	^b
CoCl ₂ (2BPDMH) ₂ ·3H ₂ O	5.08	25.1		9.3	15.1(400)	19.8
Co(NCS) ₂ (2BPDMH) ₂ ·3H ₂ O	5.29	24.8	19.8	9.3	16.5(320)	38.8
<i>Zinc complexes</i>		Lowest charge-transfer band				
ZnCl ₂ (CDDMH)	diamagnetic		27.0			2.5
ZnCl ₂ (APDMH)	diamagnetic		25.0			1.4
ZnCl ₂ (BPDMH)	diamagnetic		25.2			9.0
ZnCl ₂ (4BPDMH) ₂	diamagnetic		26.1			2.2

^aIn nitromethane. ^bInsoluble.

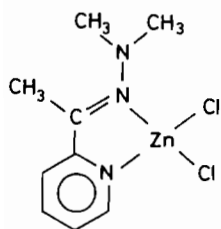
TABLE III. Some Important Infrared Bands (cm^{-1}) in Complexes of CDDMH, APDMH, 2BPDMH and 4BPDMH.

Complex	$\nu(\text{CN})_{\text{NCS}}$	$\nu(\text{C}=\text{N})$	$\nu(\text{N}-\text{N})$	$\nu(\text{CS})$	$\nu(\text{MX})$	$\nu(\text{MN})$
$\text{CoCl}_2(\text{CDDMH})$		1590	1150		320	342
$\text{CoBr}_2(\text{CDDMH})$		1587	1151		267	342
$\text{ZnCl}_2(\text{CDDMH})$		1595	1149		325	(obsc)
$\text{CoCl}_2(\text{APDMH})$		1585	1166		315, 270	340
$\text{CoBr}_2(\text{APDMH})$		1580	1160		269	340
$\text{ZnCl}_2(\text{APDMH})_2$	2088	1586	1159	800		248 (MN_{CS})
$\text{Co}(\text{NCS})_2(\text{APDMH})_2 \cdot \text{H}_2\text{O}$		1582	1159		220	
$\text{CoCl}_2(2\text{BPDMH})$		1590	1162		322, 260	356
$\text{CoBr}_2(2\text{BPDMH})$		1594	1160		275, 258	355
$\text{ZnCl}_2(2\text{BPDMH})$		1595	1161		339, 310	356
$\text{Co}(\text{NCS})_2(2\text{BPDMH})_2 \cdot 3\text{H}_2\text{O}$	2060	1586	1157	798		246 (MN_{CS})
$\text{CoCl}_2(2\text{BPDMH})_2 \cdot 3\text{H}_2\text{O}$		1582	1158		231	336
$\text{CoCl}_2(4\text{BPDMH})_2$		1610	1120		322, 299	241
$\text{CoBr}_2(4\text{BPDMH})_2$		1615	1119		262	242
$\text{ZnCl}_2(4\text{BPDMH})_2$		1612	1120		316, 295	239

magnetic zinc(II) complexes were prepared so that proton magnetic resonance spectra could be recorded. For $\text{ZnCl}_2(\text{CDDMH})$ in CDCl_3 , two triplets (at 3.34 and 2.38 δ) and a singlet (at 3.45 δ) are observed with integrated intensities of 1:1:3 in accord with the structure shown in which there are twelve equivalent methyl protons and two sets of four equivalent CH_2



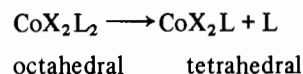
protons in the ring. Similarly the p.m.r. spectrum of $\text{ZnCl}_2(\text{APDMH})$ shows a multiplet centred at 8.78 δ and a doublet at 9.22 δ typical of a pyridine ring and two singlets at 3.44 and 3.09 δ arising from the two types of methyl groups. The overall integration is 3:1:6:3 in accord with the structure



The p.m.r. spectrum of $\text{ZnCl}_2(2\text{BPDMH})$ shows only one singlet at 3.49 δ , a multiplet centred at 8.18 and

a doublet at 9.17 δ in accord with a phenyl group replacing the unique methyl group in the above structure. The infrared spectra (Table III) support the above structural formulations. Metal-halogen stretching frequencies are in the region typically found for tetrahedral complexes and $\nu(\text{N}-\text{N})$ and $\nu(\text{C}=\text{N})$ are in the same regions as for complexes of dimethylhydrazones of 1,2-diketones [8] and hydrazones of 2-acetyl- and 2-benzoylpyridine [10] and support the proposed bonding *via* the nitrogen atom of the $\text{C}=\text{N}$ grouping.

When an excess of the pyridyl hydrazone ligands was used in complex preparation, the cobalt salts gave red solutions of the complexes (rather than green precipitates) and crystals could be deposited from these red solutions either by cooling in the refrigerator or by the addition of small amounts of diethyl ether. The red complexes (Table I) have magnetic moments and electronic spectra (Table II) clearly characterising them as containing octahedrally co-ordinated cobalt(II) in the solid state. In solution, however, the high molar absorption coefficients and shift in band positions to that typical of tetrahedral complexes clearly show that dissociation of the type



has occurred; the slight increase in conductivity is not sufficient for any significant dissociation of chloride ions or rearrangement to species such as $[\text{CoL}_2]^{2+}$ and $[\text{CoCl}_4]^{2-}$. The IR spectra (Table III) of the complexes CoCl_2L_2 (L = APDMH or 2BPDMH) show $\nu(\text{Co}-\text{Cl})$ typical for octahedral cobalt-chlorine

stretching frequencies and the thiocyanate complexes show $\nu(\text{CN})$ in the region found typically for complexes of terminally N-bonded thiocyanate [11]. Whilst $\nu(\text{Co}-\text{Cl})$ does not rule out the possibility of bridging chlorines in a polymeric structure, bridging thiocyanates show $\nu(\text{CN})$ above 2100 cm^{-1} , so these compounds CoX_2L_2 ($\text{X} = \text{Cl}, \text{NCS}$; $\text{L} = \text{APDMH}, 2\text{BPDMH}$) are probably neutral, mono-molecular bis-(chelates). It is surprising, however, that tris-(chelates) cannot be obtained from red solutions containing an excess of the ligand.

The ligand 4-benzoylpyridinedimethylhydrazine forms only 1:2 complexes with cobalt(II) and zinc(II). The cobalt(II) complexes have magnetic and spectral properties (Table II) showing them to contain tetrahedrally co-ordinated cobalt(II) both in the solid state and in nitromethane solution. The IR spectra (Table III) show strong metal-halogen stretches in the expected region for tetrahedrally co-ordinated complexes and since the complexes are non-electrolytes (Table II) they must contain unidentate ligands. Clearly unlike the other three ligands which contain the $-\text{N}=\text{C}-\text{C}=\text{N}-$ grouping, 4BPDMH cannot chelate to a metal even though it could bridge through the pyridine nitrogen and one of the hydrazone function nitrogen atoms. In our complexes, 4BPDMH appears to act as a unidentate ligand through the pyridine nitrogen atom. Thus the $\nu(\text{M}-\text{N})$ vibration is in the region found for tetrahedrally co-ordinated cobalt(II)-pyridine complexes [12] and $\nu(\text{N}-\text{N})$ occurs at a lower frequency than when bonding occurs through one of the nitrogen atoms of the hydrazone.

Experimental

Experimental techniques were as described previously [9]. Anhydrous cobalt(II) salts were prepared by dehydration of the hydrated salts at 100°C *in vacuo*. Mostly the complexes were prepared by the template method under an atmosphere of nitrogen; as different methods were used for the different ligands, examples of preparations using each ligand are described below.

Preparation of $\text{CoCl}_2(\text{CDDMH})$

Anhydrous cobalt(II) chloride (2.8 g) and cyclohexane-1,2-dione (2.4 g) were dissolved in absolute ethanol (50 cm^3) to give a blue solution. Upon addition of dimethylhydrazine (2.4 cm^3) with stirring, the solution turned green and an olive green crystalline precipitate formed. This was filtered off, washed with absolute ethanol and diethyl ether and dried *in vacuo* over silica gel. The other CDDMH complexes (Table I) were prepared similarly. Attempts to prepare complexes of nickel(II) and copper(II) halides with CDDMH by this method were unsuccessful.

Preparation of $\text{CoCl}_2(\text{APDMH})$

2-Acetylpyridine (2.5 cm^3) was added to a solution of anhydrous cobalt(II) chloride (2.9 g) in absolute ethanol (50 cm^3). The resulting dark brown solution was heated under reflux and dimethylhydrazine (1.7 cm^3) added to give a dark green solution. After heating for 1 h, dark green crystals had formed; these were filtered off, washed with absolute ethanol and diethyl ether and dried *in vacuo*.

Preparation of $\text{CoCl}_2(2\text{BPDMH})_2 \cdot 2\text{H}_2\text{O}$

2-Benzoylpyridine (2.4 g) was added to a solution of anhydrous cobalt(II) chloride (0.65 g) in absolute ethanol (20 cm^3). Dimethylhydrazine (1.0 cm^3) was added and the resulting solution heated under reflux for 4 h. Upon cooling the red solution in the refrigerator, red crystals were deposited. These were washed and dried as before. In some preparations of the bis-complexes the addition of ether to the red ethanolic solutions was necessary to induce crystallisation.

Preparation of $\text{CoCl}_2(4\text{BPDMH})_2$

The template method was not so successful for preparing complexes of 4-benzoylpyridine dimethylhydrazone and the following example illustrates the route adopted generally. 4-Benzoylpyridine (5 g) and dimethylhydrazine (2.5 cm^3) were heated together under reflux in absolute ethanol (50 cm^3) in the presence of glacial acetic acid (1 cm^3) to act as catalyst. After 4 h, the mixture was distilled *in vacuo* and a yellow oil was obtained as residue. To this oil was added a solution of anhydrous cobalt(II) chloride (1.2 g) in absolute ethanol (50 cm^3) to give a green solution and a green precipitate. The precipitate was filtered off, washed and dried as before.

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