

Cobalt(II), Nickel(II) & Copper(II) Complexes with Neutral & Deprotonated 1-Hydroxymethyl-3,5-dimethylpyrazole

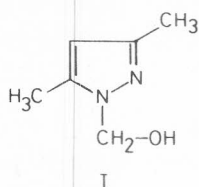
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Cobalt(II), nickel(II) and copper(II) complexes of 1-hydroxymethyl-3,5-dimethylpyrazole (DMPzCH) and its deprotonated anion (DMPzC) have been isolated and characterised in the solid state. Magnetic and electronic spectral data indicate that the stereochemistry of $\text{Co}(\text{DMPzCH})\text{X}_2 \cdot n\text{H}_2\text{O}$ is dependent on the counterion, the halo and thiocyanato species, $\text{Co}(\text{DMPzCH})\text{X}_2$ [$\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$] being tetrahedral both in solid and in solution while the corresponding nitrate, perchlorate and sulphate complexes are pseudo-octahedral. All the mono chelates of Ni(II) and Cu(II) of general composition $\text{M}(\text{DMPzCH})\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \text{NO}_3, \frac{1}{2}\text{SO}_4, \text{SCN}$) as well as the bis-species $\text{M}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ are octahedral, the anion in the mono-species being preferentially coordinated as evidenced by IR data. The pyrazolyl ring nitrogen and the carbinol oxygen of the ligand appear to be the bonding sites during complex formation. The neutral bidentate (N-O) and monoprotonic bidentate (N-O) character is envisaged in the mono- and the bis-species respectively.

Although substituted pyrazoles have long been acclaimed for their medicinal value, the coordination chemistry of pyrazole-derived ligands has been taken up only recently¹. As a part of our programme² on the coordinating properties of pyrazole-based ligands, we report herein the ligational behaviour of 1-hydroxymethyl-3,5-dimethylpyrazole(I) in acidic and basic medium towards cobalt(II), nickel(II) and copper(II) salts.



Materials and Methods

1-Hydroxy-3,5-dimethylpyrazole was prepared following a known method³, m.p. 108° (Found : C, 57.08; H, 8.01; N, 22.15. Reqd. : C, 57.14; H, 7.93; N, 22.22%); IR (KBr) : 3100-3000 (hydrogen bonded CH_2OH), 1540 ($\nu \text{C}=\text{N}$; pyrazole ring), 1060 ($\nu \text{C}-\text{O}$ of $-\text{CH}_2\text{OH}$), 800 (C-H out of plane deformation), 750 ($\delta \text{C}-\text{H}$) and 650 cm^{-1} (in-plane deformation of pyrazole ring); PMR (CDCl_3) [(TMS as internal standard in an 80 MHz Varian CFT-20 spectrometer)]: δ 2.19 (s, 3H, C_3-CH_3), 2.34 (s, 3H, C_5-CH_3), 5.38 (s, 2H, N_1-CH_2), 5.83 (s, 1H, C_4-H) 7.25 (broad s, 1H, O-H).

Preparation of complexes

$\text{M}(\text{DMPzCH})\text{X}_2 \cdot n\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4, \text{SCN}$; $n = 0, 2$)—An ethanolic solution (20 ml) of $\text{MX}_2 \cdot n\text{H}_2\text{O}^\dagger$ (0.01 mole) [in the case of metal sulphate water was used as solvent] was

added to a solution of the ligand (0.01 mol) in ethanol (25 ml). The resulting solution ($\text{pH} \sim 4$) was concentrated on a boiling water-bath and cooled to room temperature when coloured microcrystalline compounds separated out (addition of cold ether was necessary for rapid crystallisation in some cases). The compound was filtered off, washed with cold ethanol and dried in a desiccator over fused calcium chloride. The Cu(II) thiocyanate complex was prepared by reacting the Cu(II) chloride complex with an aqueous solution of potassium thiocyanate (yield 40-60%).

$\text{M}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}$)

Alcoholic solutions (25 ml) of the hydrated metal(II) chlorides (0.01 mol) and the ligand (0.02 mol, 25 ml) were mixed. On raising the pH of the solution to ~ 8 by the addition of 2N NaOH, the desired compounds separated out, which were digested for some time by heating on a boiling water-bath and then cooled to room temperature. The compounds were collected and dried as before (yield 50-75%).

Physical measurements

Cobalt content was estimated gravimetrically as anhydrous cobalt(II) sulphate, except the perchlorate complex, where the metal was estimated as the cobalt mercurithiocyanate. Nickel was estimated as nickel dimethylglyoximate and copper iodometrically. The molar conductance, magnetic susceptibilities, elec-

[†]Co(II)/Ni(II) thiocyanate solution in ethanol was prepared by mixing equivalent amounts of M(II) nitrate and potassium thiocyanate in the same solvent and filtering off the precipitated KNO_3 .

tronic and IR spectra of the complexes were recorded as described earlier⁴.

Results and Discussion

The analytical data, colour, effective magnetic moments (after diamagnetic and TIP corrections^{4a}) and molar conductance values are given in Table 1. The complexes $M(\text{DMPzCH})X_2 \cdot n\text{H}_2\text{O}$ are soluble in low molecular weight alcohols and in most of the common non-donor solvents. But the species $M(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ derived from the deprotonated ligand are practically insoluble in water and in majority of the common organic solvents.

Molar conductances of $10^{-3} M$ solutions of $M(\text{DMPzCH})X_2 \cdot n\text{H}_2\text{O}$ in methanol, except the sulphate complexes, lie in the range $50\text{--}175 \text{ ohm}^{-1} \text{ cm}^2 \text{ mo}^{-1}$, indicating their 1:1 electrolytic behaviour⁵. The conductance data can be explained in terms of partial or complete solvolysis of the complex species often containing coordinated anions in the solid state. The low conductance values of sulphate complexes characterise them as non-electrolytes, as is expected from the bridging bidentate nature of the SO_4^{2-} ion.

Cobalt(II) complexes

The room temperature magnetic moments of the deep blue halo and thiocyanate complexes of Co(II) having the composition $\text{Co}(\text{DMPzCH})X_2$ ($X = \text{Cl, Br, I, SCN}$) are in the range 3.95–4.46 B.M. These data are typical of tetrahedral cobalt(II) species⁶. The appearance of two bands in the regions $\sim 17,000$ and $\sim 8,000 \text{ cm}^{-1}$ in the electronic spectra of these complexes in solid phase may be attributed to ${}^4A_2 \rightarrow {}^4T_1(P)$ (ν_3) and ${}^4A_2 \rightarrow {}^4T_1(F)$ (ν_2) transitions respectively⁷ in tetrahedral environment. The calculated values of Dq , B and β are consistent with those of tetrahedral cobalt(II) species⁸. The electronic spectra of the Co(II) complexes in methanol exhibit bands $\sim 16,000 \text{ cm}^{-1}$ ($\epsilon > 50$). This indicates that the pseudo-tetrahedral stereochemistry persists both in solid and in solution.

The cobalt(II) perchlorate, sulphate and nitrate complexes and $\text{Co}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ have magnetic moment values in the range 4.26–4.87 B.M. (Table 1). The lower values in few cases could be attributed to an orbital singlet ground state with a distorted octahedral stereochemistry⁹. Reflectance spectral data of these complexes exhibit two bands in the regions 8,500–10,000 and 18,600–19,600 cm^{-1} assignable to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively in O_h symmetry¹⁰. The ligand field parameters Dq , B and β have been calculated. The B -values (Table 2) which are significantly less than the free ion (971 cm^{-1}) value indicate considerable overlap and delocalisation of the d -orbitals of the metal. The

electronic spectra of these complexes in DMF [$\text{Co}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ is not soluble in DMF] exhibit a band in the region 18,500–20,000 cm^{-1} (ν_3) ($\epsilon < 30$) indicating pseudo-octahedral geometry.

Nickel(II) complexes

The magnetic moment values of $\text{Ni}(\text{DMPzCH})X_2 \cdot n\text{H}_2\text{O}$ and $\text{Ni}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ lie in the range 2.79–2.92 B.M., typical of octahedral Ni(II) species, with single degenerate ${}^3A_{2g}$ (ref. 11). The diffused reflectance spectra display two bands at 8,900–10,700 and 14,700–16,400 cm^{-1} which are due to ν_1 (${}^3A_{2g} \rightarrow {}^3T_{2g}$) and ν_2 [${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$] transitions respectively in O_h symmetry¹². Excepting the perchlorate and sulphate complexes, the Ni(II) complexes also exhibit a band at 25,000 cm^{-1} which may be taken as ν_3 [${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$]. In the perchlorate and sulphate complexes this band is hidden under intense bands. The ligand field parameter Dq (taken directly from the ν_1 transition) values fall in the range 890–1040 cm^{-1} and ν_2/ν_1 lies between 1.42 and 1.69, in consonance with pseudo-octahedral Ni(II) species¹³; relatively high value of ν_2/ν_1 (viz. 1.74 for the sulphate complexes) indicates a moderate degree of tetragonal distortion¹⁴. The electronic spectra of Ni(II) complexes in DMF exhibit two bands in the regions 14,500–16,500 and 25,500–26,700 cm^{-1} which can be assigned to ν_2 and ν_3 transitions respectively in an octahedral environment. In the case of perchlorate and sulphate complexes the spectral data deviate from those in the solid phase, probably due to some degree of solvation.

Copper(II) complexes

The room temperature magnetic moment values of $\text{Cu}(\text{DMPzCH})X_2 \cdot n\text{H}_2\text{O}$ and $\text{Cu}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ lie in the range 1.66–1.81 B.M., indicating that the Cu(II) ion in these complexes is in a non-degenerate ground state¹⁵. The diffused reflectance spectra of $\text{Cu}(\text{DMPzCH})X_2 \cdot n\text{H}_2\text{O}$ and $\text{Cu}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ are characterised by a broad band in the region 12,800–14,500 cm^{-1} in O_h symmetry¹⁰. The Dq values (640–670 cm^{-1}) are in good agreement with the octahedral structure. The electronic spectra of Cu(II) in DMF [$\text{Cu}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ which is insoluble] indicate that there is no gross change in the stereochemistry of the complexes on dissolution. The shift of the spectral bands in a few cases towards lower frequency regions (bands appearing around 12,500 cm^{-1}) compared to those in the solid might be due to solvation effects.

IR spectra

The free ligand band in the region 3100–3000 cm^{-1} in the IR spectrum in KBr due to inter- and intramolecular hydrogen bonded $-\text{CH}_2\text{OH}$ group, is

shifted towards higher wavenumbers (3350-3250 cm^{-1}) in the spectra of the complexes $\text{M}(\text{DMPzCH})\text{X}_2 \cdot n\text{H}_2\text{O}$ and $\text{M}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$, indicating breaking of inter-molecular hydrogen bonding, at the same time pointing towards the possible involvement of the CH_2OH group in complexation of the metal ion through the oxygen atom².

The ν C-H of CH_2OH group appearing at 2980, 2960 and 2836 cm^{-1} in the free ligand, in general, remain unchanged upon complexation. However, δ C-H at 750 cm^{-1} in the free ligand is weakened considerably in intensity and is shifted towards lower wavenumber ($\Delta\nu \approx 70\text{-}75 \text{ cm}^{-1}$) in the complexes. The CH out-of-plane deformation mode in the free ligand at 800 cm^{-1} is shifted to a higher frequency region

Table 1—Physical Properties and Analytical Data of the Complexes

Compound	Colour	Obs. (Calc.) %			$\Lambda_M \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$	μ_{eff} (B.M.)
		M	N	Anion		
$\text{Co}(\text{DMPzCH})\text{Cl}_2$	Deep blue	22.91 (23.04)	10.7 (10.9)	27.71 (27.73)	152.0	4.05
$\text{Co}(\text{DMPzCH})\text{Br}_2$	Deep blue	16.97 (17.10)	8.09 (8.11)	46.40 (46.37)	190.5	4.46
$\text{Co}(\text{DMPzCH})\text{I}_2$	Deep blue	13.51 (13.42)	6.35 (6.37)	55.29 (55.33)	167.3	3.95
$\text{Co}(\text{DMPzCH})(\text{SCN})_2$	Deep blue	19.58 (19.60)	18.58 (18.60)	18.95* (18.99)	69.1	3.95
$\text{Co}(\text{DMPzCH})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	Pink	14.10 (14.04)	6.59 (6.66)	16.81† (16.90)	48.5	4.67
$\text{Co}(\text{DMPzCH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Pink	18.30 (18.29)	8.83 (8.82)	30.25 (30.28)	14.14	4.87
$\text{Co}(\text{DMPzCH})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Pink	17.08 (17.10)	16.20‡ (16.23)	—	46.5	4.26
$\text{Co}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$	Pink	16.95 (17.00)	16.10 (16.13)	—	—	4.67
$\text{Ni}(\text{DMPzCH})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	Light green	19.90 (19.93)	9.59 (9.62)	24.34 (24.39)	56.0	2.95
$\text{Ni}(\text{DMPzCH})\text{Br}_2 \cdot 2\text{H}_2\text{O}$	Light blue	15.20 (15.22)	7.32 (7.34)	42.00 (41.99)	60.5	2.91
$\text{Ni}(\text{DMPzCH})\text{I}_2 \cdot 2\text{H}_2\text{O}$	Brown	12.19 (12.33)	5.85 (5.9)	53.56 (53.58)	106.1	2.81
$\text{Ni}(\text{DMPzCH})(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	Light blue	17.24 (17.26)	16.64 (16.66)	—	58.7	2.79
$\text{Ni}(\text{DMPzCH})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	Blue	13.90 (13.84)	6.65 (6.68)	16.92† (16.94)	173.6	2.86
$\text{Ni}(\text{DMPzCH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Blue	18.36 (18.35)	8.81 (8.86)	30.21 (30.37)	6.05	2.81
$\text{Ni}(\text{DMPzCH})(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	Light blue	16.85 (16.86)	16.27‡ (16.27)	—	—	2.77
$\text{Ni}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$	Light blue	16.75 (16.76)	16.16 (16.18)	—	—	2.81
$\text{Cu}(\text{DMPzCH})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$	Brown	21.36 (21.41)	9.40 (9.44)	23.89 (23.89)	80.3	1.81
$\text{Cu}(\text{DMPzCH})\text{Br}_2 \cdot 2\text{H}_2\text{O}$	Green	16.45 (16.47)	7.24 (7.26)	41.40 (41.50)	75.6	1.72
$\text{Cu}(\text{DMPzCH})(\text{SCN})_2 \cdot 2\text{H}_2\text{O}$	Green	18.60 (18.59)	16.36* (16.39)	18.72‡ (18.74)	65.32	1.78
$\text{Cu}(\text{DMPzCH})\text{SO}_4 \cdot 2\text{H}_2\text{O}$	Blue	18.72 (19.75)	8.50 (8.70)	29.85 (29.86)	14.2	1.66
$\text{Cu}(\text{DMPzCH})(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$	Blue	15.00 (14.95)	6.55 (6.59)	16.5† (16.7)	109.2	1.76
$\text{Cu}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$	Blue	18.01	15.86	—	—	1.81

*Including nitrogen present in thiocyanate.

†Percentage of chlorine.

‡Including nitrogen present in nitrate.

Table 2—Ligand Field Parameters of the Complexes

Complex	Dq	B	β
Co(DMPzCH)Cl ₂	454	745	0.76
Co(DMPzCH)Br ₂	455	730	0.75
Co(DMPzCH)I ₂	—	—	—
Co(DMPzCH)(SCN) ₂	458	750	0.77
Co(DMPzCH)(ClO ₄) ₂ ·2H ₂ O	999	759	0.78
Co(DMPzCH)SO ₄ ·2H ₂ O	959	826	0.85
Co(DMPzCH)(NO ₃) ₂ ·2H ₂ O	890	873	0.90
Co(DMPzC) ₂ ·2H ₂ O	999	759	0.78
Ni(DMPzCH)Cl ₂ ·2H ₂ O	890	833	0.77
Ni(DMPzCH)Br ₂ ·2H ₂ O	1070	546	0.50
Ni(DMPzCH)(SCN) ₂ ·2H ₂ O	900	880	0.81
Ni(DMPzCH)I ₂ ·2H ₂ O	980	820	0.75
Ni(DMPzCH)(ClO ₄) ₂ ·2H ₂ O	1040	755	0.70
Ni(DMPzCH)SO ₄ ·2H ₂ O	860	746	0.70
Ni(DMPzCH)(NO ₃) ₂ ·2H ₂ O	1020	646	0.60
Ni(DMPzC) ₂ ·2H ₂ O	960	613	0.57
Cu(DMPzCH)Cl ₂ ·2H ₂ O	699	—	—
Cu(DMPzCH)Br ₂ ·2H ₂ O	735	—	—
Cu(DMPzCH)(SCN) ₂ ·2H ₂ O	740	—	—
Cu(DMPzCH)SO ₄ ·2H ₂ O	640	—	—
Cu(DMPzCH)(ClO ₄) ₂ ·2H ₂ O	760	—	—
Cu(DMPzC) ₂ ·2H ₂ O	737	—	—

($\Delta\nu \approx 20-40 \text{ cm}^{-1}$) on complexation. These observations indicate bonding of the metal ion through the CH₂OH group¹⁶. $\nu\text{C-O}$ of the free ligand ($\sim 1060 \text{ cm}^{-1}$) is shifted ($\Delta\nu \approx 20-30 \text{ cm}^{-1}$) to lower wavenumber in the spectra of the complexes, $\text{M}(\text{DMPzCH})\text{X}_2 \cdot n\text{H}_2\text{O}$, indicating coordination of the metal ion through oxygen of C-O¹⁶. In $\text{M}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$, the corresponding bands appear in the region $1100-1120 \text{ cm}^{-1}$, which shift to higher wavenumbers in the complexes ($\Delta\nu \approx 40-60 \text{ cm}^{-1}$) due to ionisation of the proton of CH₂OH group, resulting in the strengthening of the $-(\text{C-O})$ band¹⁷.

The free ligand bands at 1540 and 650 cm^{-1} assignable to $\nu(\text{C}=\text{N})$ and in-plane deformation of the pyrazole ring respectively, are shifted to higher wavenumbers ($\Delta\nu \approx 20-40$ and $15-30 \text{ cm}^{-1}$ in $\nu\text{C}=\text{N}$ and in-plane deformation) in both type of complexes, suggesting the tertiary nitrogen atom of the pyrazole ring as a possible bonding site¹⁸. New bands which are absent in the far IR spectrum of the free ligand appear in the metal complexes at 400 (ms) and 250 cm^{-1} (ms) assignable to the $\nu\text{M-O}$ (ref. 19) and $\nu\text{M-N}$ (ref. 20), respectively. The diagnostic IR bands of the polyatomic anions (X) indicate clearly the monodentate nature of ClO₄ (ref. 21) [bands appearing at $\sim 1150-1120$ and $\sim 1090 \text{ cm}^{-1}$ are the split components of $\nu(\text{Cl-O})$ in C_{3v} symmetry], NO₃ (ref. 22) [bands at ~ 1380 and $\sim 1300 \text{ cm}^{-1}$ are the split components of ν_3 ; ~ 800 (ν_2) in C_{2v} symmetry] and NCS (ref. 23) [(N-bonded) $\sim 2090 \nu(\text{C}=\text{N})$; $\sim 790 \text{ cm}^{-1}$ ($\nu\text{C-S}$)]. The sulphate group on the other hand is

present as a bridging bidentate one²⁴ [~ 1100 ; ~ 1045 ; $\sim 1025 \text{ cm}^{-1}$ split components of ν_3 ; $\sim 900 \text{ cm}^{-1}$ (ν_1) in C_{2v} symmetry].

It appears, therefore, from the above discussion that the ligand 1-hydroxymethyl-3,5-dimethylpyrazole exhibits a neutral bidentate NO donor in $\text{M}(\text{DMPzCH})\text{X}_2 \cdot n\text{H}_2\text{O}$ complexes where the counterion (X) is preferably coordinated, while at higher pH (~ 8) the same ligand shows a monoprotic bidentate NO character in forming $\text{M}(\text{DMPzC})_2 \cdot 2\text{H}_2\text{O}$ which are probably polymeric octahedral through intermolecular bridging. However, in the absence of cryomagnetic and ESR data, the suggestion regarding the polymeric nature of complexes is highly conjectural.

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