IRON(II) COMPLEXES OF PYRAZOL-4,5-DIONE-5-OXIMES

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Abstract—The complexes $Fe(po)_2 H_2O$, $Fe(Ppo)_2 H_2O$ and $Fe(Ppo)_2 2py$, where poH = 3 - methyl - 4 - oxime - 1H - pyrazole - 4,5 - dione and PpoH = 3 - methyl - 4 - oxime - 1 - phenyl - 1H - pyrazole - 4,5 - dione, have been prepared. The magnetic susceptibilities and Mössbauer spectra of the complexes have been investigated.

The reactions of 2-nitrosophenols (mono-oximes of 1,2-quinones) (LH) with metal salts or with metal carbonyls give neutral metal complexes of type ML_n (n = 2 or 3).¹⁻³ In certain cases deoxygenation of the ligand can occur to give heterocyclic or other organic products. We now report on the reactions of the related ligands 3 - methyl - 4 - oxime - 1H - pyrazole - 4,5 - dione (poH) (1; R = H, R' = CH₃) and 3 -



methyl - 4 - oxime - 1 - phenyl - 1H - pyrazole - 4,5 dione (PpoH) (1; $R = C_6H_5$, $R' = CH_3$) with iron(II) ammonium sulphate and with iron(O) pentacarbonyl. We also report on the properties and structure of the metal complexes which arise from these reactions. Complexes of copper(II), nickel(II), zinc(II), cadmium(II) and magnesium(II) derived from ligands of type 1 (R = H, C_6H_5 , $4-(NO_2)C_6H_4$, $4-ClC_6H_4$, $2,4-(NO_2)_2C_6H_3$; R' = H, CH_3 , C_6H_5) have been reported earlier.⁴⁻⁶

EXPERIMENTAL

The ligands were prepared as described in the literature.⁷

Interaction of 3 - methyl - 1 - phenyl - 4 - oxime - 1H - pyrazole - 4,5 - dione or 3 - methyl - 4 - oxime 1H - pyrazole - 4,5 - dione with iron(II) ammonium sulphate

3 - Methyl - 1 - phenyl - 4 - oxime - 1H - pyrazole - 4,5 dione (2.0 g, 2 mol equiv.) and iron(II) ammonium sulphate (1.9 g, 1 mol equiv.) were stirred in ethanol-water (2:1) (120 cm³) (1 hr). Turquoise bis(3 - methyl - 1 - phenyl -4 - oximato - 1H - pyrazole - 4,5 - dione)iron(II) monohydrate (1.4 g, 59%), (Found: C, 50.2; H, 4.1; Fe, 11.7; N, 17.1. $C_{20}H_{18}FeN_6O_5$ requires: C, 50.2; H, 3.8; Fe, 11.7; N, 17.6%), was filtered off, washed with water (2 × 100 cm³) and ethanol (2 × 100 cm³) and dried at 30°C/0.1 mm.

Unchanged 3 - methyl - 4 - oxime - 1H - pyrazole - 4,5 - dione (88%) (identified by IR) was recovered after stirring (4 hr) with the iron(II) salt in ethanol-water.

Interaction of 3 - methyl - 4 - oxime - 1H - pyrazole - 4,5 - dione with iron pentacarbonyl

3 - Methyl - 4 - oxime - 1H - pyrazol - 4,5 - dione (2.51 g, 1 mol equiv.) and iron pentacarbonyl (19.4 g, 5 mol equiv.) were heated under reflux for 12 hr in dry tetrahydrofuran (100 cm³) under nitrogen. The mixture was filtered to give dark green bis(3 - methyl - 4 - oximato - 1H - pyrazol - 4,5 dione)iron(II) - monohydrate (1.49 g, 54%). (Found: C, 29.9; H, 2.8; Fe, 17.1, N, 25.9) C₈H₁₀FeN₆O₆ requires: C, 29.5; H, 3.1; Fe, 17.1; N, 25.8%) which was washed with tetrahydrofuran and dried at 30°C/0.1 mm. The washings were concentrated and filtered to give orange 2,4 - dihydro -4 - (5 - hydroxy - 3 - methyl - 1H - pyrazol - 4 - yl)imino 5 - methyl - 3H - pyrazole - 3 - one (0.14 g, 8%). (Found C, 47.1; H, 4.9; N, 33.6%; C₈H₉N₅O₂ requires: C, 46.9; H, 4.8; N, 33.8%), m.p. 265-67°C sub.; m/e 207 (M⁺).

Interaction of 3 - methyl - 1 - phenyl - 4 - oxime - 1H - pyrazole - 4,5 - dione with iron pentacarbonyl

3 - Methyl - 1 - phenyl - 4 - oxime - 1H - pyrazole - 4,5 dione (2.04 g, 2 mol equiv.) and iron pentacarbonyl (0.98 g, l mol equiv.) were heated under reflux for 12 hr under nitrogen in dry tetrahydrofuran (100 cm³). Chromatography of the mixture (silica gel) gave, with toluene as eluant 2,4 dihydro - 4 - (5 - hydroxy - 3 - methyl - 1 - phenyl - 1H pyrazol - 4 - yi) - imino - 5 - methyl - 1 - phenyl - 1H pyrazol - 4 - yi) - imino - 5 - methyl - 1 - phenyl - pyrazol 3 - one (0.41 g 66%), m.p. 185-7°C (*lit.*,⁸ 183°C), (Found: C, 67.1; H, 5.1; N, 19.2%). Calc. for C₂₀H₁₇N₅O₂: C, 66.8; H, 4.8; N, 19.5%), *m/e* 359 (M⁺). Further elution with toluene gave 1,2,5 - oxadiazole[3,4-d] - 6 - methyl - 4 phenyl - 4H - pyrazole (0.04 g, 6%), m.p. 86-8°C (*lit.*,⁹ 91°C), *m/e* 200 (M⁺). Methanol eluted *bis*(5 - methyl - 1 phenyl - 4 - oximato - 1H - pyrazol - 4,5 - dione)iron(II) hydrate, (0.11 g, 14%) (identified by IR).

Interaction of bis(3 - methyl - 1 - phenyl - 4 - oximato 1H - pyrazole - 4,5 - dione)iron(II) - monohydrate with pyridine

Bis(3 - methyl - 1 - phenyl - 4 - oximato - 1H - pyrazole - 4,5 - dione)iron(II) - monohydrate (2.6 g) and pyridine (10 cm³) were stirred for 24 hr. Bis(3 - methyl - 1 - phenyl - 4 - oximato - 1H - pyrazole - 4,5 - dione)iron(II) - dipyridine (2.7 g, 79%) (Found: C, 57.7; H, 4.4; Fe, 8.6; N, 17.7. C₃₀H₂₆FeN₈O₄ requires C, 58.2; H, 4.2; Fe, 9.0; N, 18.1%) was filtered off, washed with diethyl ether (2 × 50 cm³) and dried at 30°C/0.1 mm.

Thermal gravimetric analysis data for Fe(Ppo)₂·2py

Weight of sample: 206 mg. Weight loss: 55 mg (Calc. for 2 mol of pyridine per mol of adduct: 53 mg). Temperature of loss: $172-8^{\circ}$ C.

Measurements

Magnetic susceptibility and thermogravimetric analysis data, also IR and NMR spectra were obtained as described earlier.¹ Mössbauer spectra were recorded on a constant acceleration Mössbauer spectrometer (J and P Engineering, Reading) using a ⁵⁷Co source in a rhodium matrix (Spire Corporation). The velocity calibration was based on the inner four lines of the spectrum of natural iron.

RESULTS AND DISCUSSION

The reaction of iron(II) ammonium sulphate with PpoH in aqueous ethanol gave a turquoise complex of stoichiometry Fe(Ppo)₂·H₂O. In contrast poH failed to react with the iron(II) salt under similar conditions. However, the complex Fe(po)₂·H₂O was obtained along with some 2,4 - dihydro - 4 - (5 - hydroxy - 3 methyl - 1H - pyrazol - 4 - yl)imino - 5 - methyl - 3H pyrazol - 3 - one (2; R = H) from the reaction of the oxime with iron pentacarbonyl. The reaction of iron pentacarbonyl with PpoH afforded mainly 2,4 - dihy-





dro - 4 - (5 - hydroxy - 3 - methyl - 1 - phenyl - 1 \underline{H} pyrazol - 4 - yl)imino - 5 - methyl - 2 - phenyl - 3 \overline{H} pyrazol - 3 - one (2; $R = C_6H_5$), together with 1,2,5 oxadiazole[3,4-d] - 6 - methyl - 4 - phenyl - 4 \underline{H} pyrazole (3) and Fe(Ppo)₂·H₂O. The formation of the organic products can be rationalised in terms of deoxygenation of the protonated ligands as discussed for analogous reactions of complexes of quinone mono-oximes.^{10,11}

The complex $Fe(Ppo)_2 H_2O$ reacted with pyridine to give $Fe(Ppo)_2 2py$. The thermal gravimetric analysis of the adduct showed that pyridine (2 mol/mol adduct) was lost at *ca*. 175°C. The room temperature magnetic moments (Table 1) of the hydrates and of



Table 1.	Magnetic	and	Mössl	bauer	data
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Fe(Ppo) ₂ ·H ₂ O										$\delta (\mathrm{mm} \mathrm{s}^{-1})^{\dagger}$	$\Delta (\mathrm{mm} \mathrm{s}^{-1})^{\dagger}$
$ \begin{array}{c} T (K) \\ 10^{6} \chi_{A} \\ \mu_{\text{eff.}} (B.M) \\ -\theta (K) \end{array} $	363 10443 5.51 280	333 11202 5.47	303 11383 5.26	272 12032 5.13	243 12789 4.99	214 13481 4.80	184 14437 4.61	154 14920 4.28	124 16367 4.03	1.19 1.18	2.58 at 300 K 2.55 at 75 K
Fe(Ppo) ₂ ·2py											
$ \begin{array}{c} T (K) \\ 10^{6} \chi_{A} \\ \mu_{eff} (B.M) \\ -\theta (K) \end{array} $	363 10399 5.50 0	335 11402 5.53	303 12515 5.51	273 13431 5.42	243 15650 5.52	213 17870 5.52	184 20688 5.52	153 24645 2.49	124 30768 5.53	1.10	2.51 at 300 K
Fe(po) ₂ ·H ₂ O											
$ \begin{array}{c} T (K) \\ 10^{6} \chi_{A} \\ \mu_{eff.} \\ -\theta (K) \end{array} $	363 10402 5.50 316	333 11121 5.45	302 11665 5.31	273 11828 5.09	244 12297 4.90	214 12858 4.69	183 13886 4.51	153 14771 4.26	123 16096 3.99	1.03 1.14	2.61 at 300 K 262 at 75 K

†The isomer shifts (δ) are given relative to iron foil. The errors in δ and Δ are of the order 0.02 and 0.03 mm s⁻¹ respectively.

the pyridine adduct lie between 5.2 B.M. and 5.4 B.M. and are indicative of high-spin iron(II).

The magnetic behaviour of the complexes was measured at variable field strength and at variable temperature (Table 1). All complexes follow the Curie-Weiss Law. The decreasing magnetic moment with temperature of the hydrates and their large negative Weiss constants indicate antiferromagnetic behaviour and suggest association (4). However the experimental data do not rule out the possibility of spin-orbit coupling. Some indirect support for association is provided by the insolubility of the complexes and the contrasting magnetic behaviour of the pyridine adduct. The room magnetic moment, the negligible Weiss constant and the lack of significant variation of magnetic moment within the temperature range used all suggest that the pyridine adduct is monomeric. The value of $\theta = 0$ for Fe(Ppo)₂·2py suggests that the pyridine adduct is magnetically dilute, indicating a pseudooctahedral structure. The Mössbauer parameters of all the complexes (Table) indicate that the materials are essentially free from iron(III) impurities, and are in accord with high-spin iron(II), and the structural suggestions.¹²

The high spin character of the iron complexes suggests that the ligand field exerted by po^- or Ppo^- is weak. This contrasts with the high ligand-field character of quinoneoximato ligands and is probably a consequence of the limited conjugation within the chelated po^- or Ppo^- ligands.

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