

Copper(II), Nickel(II) & Palladium(II) Chelates of 2-(Phenylazo)-1,3-diketones

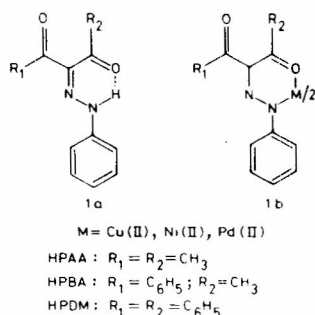
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On the basis of IR and PMR spectral evidences phenylazo derivatives of acetylacetone, benzoylacetone and dibenzoylmethane are shown to exist predominantly in hydrazone form, and to yield copper(II), nickel(II) and palladium(II) chelates through coordination of their hydrazone nitrogen and one of the acyl oxygens. EPR spectra of the copper(II) chelates indicate that the metal ligand bonds have considerable covalent character, and that *d*-electron delocalisation from the central atom to the chelate ring is relatively more in the metal chelate of phenylazoacetylacetone. That the decreased delocalisation in the other two chelates is the result of destabilising cross conjugation by benzoyl group, is evident from the order of stability of the chelates determined *pH*-metrically and polarographically.

Azo-hydrazone tautomerism of arylazo derivatives of β -dicarbonyl compounds has evoked considerable interest and controversy in the past¹⁻⁵. In the present investigation, 3-(phenylazo)-2,4-pentanedione (phenylazoacetylacetone, HPAA), 2-(phenylazo)-1-phenyl-1,3-butanedione (phenylazobenzoylacetone, HPBA) and 2-(phenylazo)-1,3-diphenyl-1,3-propanedione (phenylazodibenzoylmethane, HPDM) have been shown, on the basis of their IR and PMR spectra, to exist predominantly in the hydrazone form (Ia). Copper(II), nickel(II) and palladium(II) chelates synthesised have been characterised as derivatives of this form, the ligands acting as monobasic bidentate leaving an acyl group free, as in Ib.



Materials and Methods

The azo compounds were prepared as reported¹. For preparing copper(II) and nickel(II) complexes, a solution of the metal(II) acetate (2.5 mmol, 15 ml) was added to a stirred solution of the ligand in ethanol (5 mmol, 50 ml), concentrated on a water-bath to about 25 ml and then cooled in ice. The precipitated complex was filtered, washed with water, and recrystallised from hot benzene. Palladium(II) complexes were prepared by adding a solution of palladium(II)

chloride in acetone (0.5 mmol, 10 ml) to a boiling solution of the ligand in ethanol (1 mmol, 25 ml). The precipitate obtained on cooling the solution in ice was filtered off, washed with ethanol and recrystallised from hot ethanol.

Molar conductances of the complexes were determined on a Toshniwal conductivity bridge using 10⁻³ M solutions in ethanol. A Gouy type magnetic balance was used to measure magnetic moment at 28 ± 0.2°C, using Hg[Co(CNS)₄] as standard.

An Elico recording polarograph was used for polarographic stability comparison. Solutions (10⁻³ M) of the complexes were prepared in aqueous pyridine (50% v/v) containing KNO₃ (10⁻¹ M) as supporting electrolyte. usual precautions were observed while recording polarograms using a saturated calomel electrode as reference electrode.

pH measurements were made on an Elico digital *pH*-meter using a glass electrode. Acid dissociation constants of the ligands were determined by titrating 0.05 M solution of KOH against 0.1 M solution of the ligand, both in aqueous dioxane (50% v/v). The *pH* at half-neutralisation⁶ was taken as *pK_a*. Formation constants of the copper(II) chelates were determined by the method of Bjerrum-Calvin as employed by Harries *et al.*^{6,7}

Results and Discussion

All the metal complexes behave as non-electrolytes (sp. cond. < 10 ohm⁻¹ cm⁻² mol⁻¹). Copper(II) complexes show normal magnetic moments in the range 1.75-1.80 B.M. Nickel(II) and Pd(II) complexes are diamagnetic. The compositions of the metal complexes arrived at on the basis of their elemental analyses, magnetic, and molar conductance data are given in Table I.

Table 1—Analytical and Physical Data of Copper(II) Nickel(II) and Palladium(II) Complexes of Phenylazo- β -diketones

Complex	Yield (%)	m.p. (°C)	Colour	Found (calc.) (%)			
				C	H	N	Metal*
[Cu(PAA) ₂]	67	190	Dark green	55.03 (56.24)	4.51 (4.69)	11.04 (11.92)	13.24 (13.51)
[Cu(PBA) ₂]	65	290	Dark green	63.58 (64.69)	4.43 (4.35)	9.63 (9.44)	10.80 (10.10)
[Cu(PDM) ₂]	50	268	Greenish black	69.58 (70.25)	3.91 (4.18)	8.72 (7.80)	8.17 (8.86)
[Ni(PAA) ₂]	58	225	Red	54.68 (56.80)	4.23 (4.73)	11.21 (12.05)	—
[Ni(PBA) ₂]	52	240	Red	63.12 (65.22)	4.98 (4.42)	9.47 (10.63)	—
[Ni(PDM) ₂] ^f	48	185	Red	67.95 (70.71)	4.86 (4.21)	8.91 (9.51)	—
[Pd(PAA) ₂]	74	235	Brownish yellow	50.16 (51.52)	4.85 (4.29)	9.92 (10.92)	—
[Pd(PBA) ₂]	70	210	Deep brown	58.94 (60.34)	4.51 (4.08)	9.03 (9.79)	—
[Pd(PDM) ₂]	65	225	Black	67.78 (66.25)	4.21 (3.95)	8.01 (8.79)	—

*Cu content determined by atomic absorption spectrometry (Perkin-Elmer 257 instrument)

IR spectra of the three ligands recorded in nujol on a Perkin-Elmer model 257 spectrophotometer exhibit two strong bands each (HPAA 1675, 1625; HPBA 1652, 1625; HPDM 1650, 1618 cm^{-1}) in the region 1680-1600 cm^{-1} . From their high intensity these bands are easily recognised as carbonyl bands, and from their positions it is evident that one of the bands is due to conjugated free carbonyl, and the other due to hydrogen bonded carbonyl⁸.

These spectral data clearly indicate that it is the acetyl carbonyl of phenylazobenzoylacetone that is hydrogen bonded with the hydrazone NH. In conformity with this internally hydrogen bonded structure (Ia), spectra of the compounds display a very broad band in the region 3375-2400 cm^{-1} .

Spectra of the metal chelates are compatible with the structure that would result, if the chelated hydrogen of the ligands is replaced by metal ion (structure Ib). Thus, the position of the free carbonyl bands of the ligands is only marginally altered in the spectra of their metal chelates. Instead of the free ligand bands at $\sim 1620 \text{ cm}^{-1}$ (due to hydrogen bonded carbonyl) spectra of the metal complexes exhibit another strong band around 1550 cm^{-1} , assignable⁹ to $\nu\text{C}=\text{O}\dots\text{M}$. A weak band attributable to conjugated $\nu(\text{C}=\text{N})$, appears at 1615 cm^{-1} in the spectra of all the metal chelates. In the spectra of the ligands this band is presumably masked by the strong absorption (occurring in the same region) of hydrogen bonded carbonyl.

The broad free ligand bands in the region 3375-2400

cm^{-1} disappear in the spectra (KBr pellet) of the metal chelates, and instead a weak band around 3050 cm^{-1} assignable to $\nu\text{C}-\text{H}$ (aromatic) appears in the spectra of the chelates. Metal chelates of phenylazo derivatives of acetylacetone and benzoylacetone also exhibit weak absorptions in the region 2950-2840 cm^{-1} , due to $\nu\text{C}-\text{H}$ (methyl group).

In conformity with the structure proposed, PMR spectrum of phenylazoacetylacetone (in CDCl_3) and of its palladium(II) chelate (in $\text{DMSO}-d_6$), recorded on a Varian XL-100 FT instrument (TMS internal reference), displayed two methyl proton signals of equal intensity each at δ 2.48 and 2.62, and δ 2.35 and 2.45 respectively. Apart from multiplets around δ 7.5 for aromatic protons, the three phenylazo- β -diketones showed also a low field signal for the chelated hydrazone NH. Whereas the PMR spectra of phenylazo derivatives of acetylacetone and benzoylacetone exhibited this signal at δ 14.74 and 14.70 respectively; in phenylazodibenzoylmethane NH appears at δ 13.55. This shift indicates that in phenylazobenzoylacetone, it is the acetyl carbonyl that is hydrogen bonded, in conformity with the IR data. The PMR spectra of the metal chelates did not show this low field signal, thus confirming that the chelated hydrogen of the hydrazone is replaced by palladium(II).

In conformity with the structure arrived at above, the three ligands do not answer the colour test for enols with Fe^{3+} ion, even on boiling. Since oxygen-coordination alone is unlikely to bring about spin-

Table 2—EPR Spectral Data, Formation Constants, Half-wave Potentials and Far IR Spectral Data of Copper(II) Chelates of Phenylazo- β -diketones

Complex	EPR spectra*		Formation constants			$E_{1/2}$ (V) first wave	Far IR data (cm^{-1})	
	A_{Cu}	g_{av}	$\log k_1$	$\log k_2$	$\log k_{\text{av}}$		$\nu(\text{Cu}-\text{N})$	$\nu(\text{Cu}-\text{O})$
[Cu(PAA) ₂]	66.5	2.207	8.89	7.81	8.35	-0.32	555	428
[Cu(PBA) ₂]	67.5	2.144	8.68	7.82	8.25	-0.31	550	425
[Cu(PDM) ₂]	72.5	2.126	8.58	7.24	8.21	-0.24	548	410

*DPPH as the reference

pairing¹⁰ of nickel(II), the observed diamagnetism of nickel(II) chelates is a strong indication of nitrogen-coordination as in Ib.

EPR spectra of the copper(II) chelates recorded in acetone, on a Varian E-4 (X-band) instrument, reveal four sets of five lines each. Coupling of the electronic spin with the spin of the metal nucleus ($I=3/2$ for ⁶³Cu) can cause four lines. Hyperfine splitting of these four lines by two equivalent nitrogen atoms can lead to the observed spectra. These spectra therefore, clearly indicate that a nitrogen atom of each ligand moiety is bonded to the metal. The g -values of the metal complexes quoted in Table 2 reveal that the metal-ligand bonds have considerable covalent character^{11,12}.

The A_{Cu} values observed (Table 2) indicate that delocalisation of metal d -electrons to the chelate ring is greater in phenylazoacetylacetone chelate. Cross conjugation by benzoyl group¹³ seems to destabilise the metal chelates of phenylazobenzoylacetone and phenylazodibenzoylmethane, thus rendering electron delocalisation less facile. This view is fully substantiated by the order of stability of the three copper(II) chelates, as judged from their formation constants and polarographic reduction potentials¹⁴ (Table 2). It may be noted that this stability order is to

be expected from the observed pK_a values of the ligands (9.25, 9.05 and 8.95 respectively for the ligands derived from acetylacetone, benzoylacetone and dibenzoylmethane). The $\nu(\text{Cu}-\text{N})$ and $\nu(\text{Cu}-\text{O})$ values³ of the three chelates are also in conformity with the above stability order (Table 2).

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