

## Copper(II), nickel(II), palladium(II) and iron(III) complexes of 2-(3-phthalhydrazidylazo)-1,3-diketones

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**Abstract.** Neutral complexes of three phthalhydrazidylazo-1,3-diketones [phthalhydrazidylazo-acetylacetone ( $H_2PAA$ ), -benzoylacetone ( $H_2PBA$ ) and -dibenzoylmethane ( $H_2PDM$ )] with Cu(II), Ni(II), Pd(II) and Fe(III) have been synthesised and characterized on the basis of their analytical data, magnetic moment, molar conductance and IR and  $^1H$  NMR spectral data. Dibasic tridentate coordination of the ligands is brought out by the above spectral data. Half-wave potentials and far IR spectral data of the Cu(II) complexes indicate that the  $H_2PAA$  complex is the most stable. Mössbauer spectra of the Fe(III) complexes reveal that delocalisation of the metal  $d$  electrons with the chelate ring decreases with increasing capability of the pendant groups of the ring for cross conjugation.

**Keywords.** Phthalhydrazidylazo-1,3-diketones; transition metal complexes; IR spectra; NMR spectra; Mössbauer spectra; stability of complexes.

### 1. Introduction

Extensive literature is available on metal chelates of *o*, *o'*-disubstituted diarylazo compounds, which have significant application as stable dyestuffs and as analytical reagents (Venkataraman 1952; Price 1970). However, very few reports exist on metal complexes of azo dyes formed from heterocyclic amines via diazotization, and coupling with the reactive methylene group of  $\beta$ -diketones. Details of the synthesis and characterization of Cu(II), Ni(II), Pd(II) and Fe(III) complexes of three phthalhydrazidylazo-1,3-diketones prepared from 3-aminophthalhydrazide (the chemiluminescent organic compound well-known by its trivial name 'luminol') are brought out in this paper, the 1,3-diketones used being acetylacetone, benzoylacetone and dibenzoylmethane.

### 2. Experimental

#### 2.1 Preparation of 2-(3-phthalhydrazidylazo)-1,3-diketones

Phthalhydrazidylazoacetylacetone ( $H_2PAA$ ), phthalhydrazidylazo-benzoylacetone ( $H_2PBA$ ) and phthalhydrazidylazodibenzoylmethane ( $H_2PDM$ ) were prepared as reported earlier (Thankarajan *et al* 1986).

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## 2.2 Preparation of metal complexes

Copper(II) complexes were prepared by adding an aqueous solution (15 ml) of the metal(II) acetate (2.5 mmol) to a stirred ethanolic solution (100 ml) of the ligand (2.5 mmol) maintained at  $\sim 60^\circ\text{C}$ . After refluxing the mixture for 2 hr, the precipitated complex was filtered, washed successively with water, ethanol and diethyl ether, and then dried in vacuum. For preparing palladium(II) complexes, palladium(II) chloride (0.215 g, 1 mmol) dissolved in acetone (25 ml) was added to a hot and stirred solution (50 ml) of the ligand (1 mmol). The mixture was refluxed for about 1 hr, the precipitated complex filtered, washed with ethanol, and recrystallised from hot ethanol.

Iron(III) complexes were prepared by mixing an ethanolic solution (10 ml) of iron(III) chloride hexahydrate (0.135 g, 5 mmol) with a hot and stirred solution of the ligand (5 mmol) in ethanol (50 ml). The deep brown precipitate formed on adding sodium acetate (0.1 g) was filtered, washed with very dilute acetic acid and ethanol, and then dried in vacuum.

## 2.3 Physical measurements

Molar conductance was measured at  $28 \pm 0.2^\circ\text{C}$  in ethanol ( $10^{-3}$  M) using a Toshniwal conductivity bridge. Magnetic susceptibilities were determined at room temperature on a Gouy type magnetic balance. Infrared spectra (Nujol mull and KBr disc) were recorded on a Perkin-Elmer 257 spectrometer, and far IR spectra (CsI disc) on a polytech FIR spectrometer.  $^1\text{H}$  NMR spectra ( $\text{DMSO-}d_6$ ) were obtained from a Varian XL-100 FT NMR spectrometer. For recording Mössbauer spectra (natural iron as reference), a constant acceleration Mössbauer spectrometer ECIL MBS 35 coupled to a multichannel analyser NCA 38 was used. Polarograms were recorded in aqueous pyridine (50% v/v) using  $\text{KNO}_3$  as supporting electrolyte on an Elico pen recording polarograph. Carbon, hydrogen and nitrogen percentages reported are by microanalyses, and metal contents by standard gravimetric procedures.

## 3. Results and discussion

All complexes behave as non-electrolytes (specific conductance  $< 10 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ), and do not contain the anion of the metal salt used for preparing them. Nickel(II) and palladium(II) complexes are diamagnetic, while copper(II) complexes show normal magnetic moments of 1.78–1.82 B.M. Magnetic moment of the iron(III) complexes are in the high spin range of 5.90–5.95 B.M. Based on elemental analysis, molar conductance and magnetic moment data the complexes are represented as in table 1.

### 3.1 IR spectra

Infrared and  $^1\text{H}$  NMR spectral data indicate that the three phthalhydrazidylazo- $\beta$ -diketones exist as hydrogen bonded hydrazoneenol, as in the structure I (Thankarajan *et al* 1986). Thus, while the IR spectrum of  $\text{H}_2\text{PAA}$  showed a strong band at  $1672 \text{ cm}^{-1}$  for free acetyl carbonyl, spectra of  $\text{H}_2\text{PBA}$  and  $\text{H}_2\text{PDM}$  showed

**Table 1.** Analytical data and other details about the metal complexes of 2-(3-phthalhydrazidylazo)-1,3-diketones.

Complex	Yield (%)	M.P. (°C)	$\mu_{\text{eff}}$ (B.M.)	Found (Calcd.) (%)			
				C	H	N	Metal
[Cu(PAA) (H <sub>2</sub> O)]	65	a	1.82	42.01 (42.44)	2.98 (3.27)	14.86 (15.23)	17.12 (17.28)
[Cu(PBA) (H <sub>2</sub> O)]	58	a	1.79	49.68 (50.28)	3.13 (3.25)	12.86 (13.03)	14.56 (14.79)
[Cu(PDM) (H <sub>2</sub> O)]	55	a	1.78	55.73 (56.15)	3.09 (3.26)	11.01 (11.39)	12.78 (12.93)
[Ni(PAA) (H <sub>2</sub> O)]	65	328	D	42.59 (43.01)	3.20 (3.31)	15.10 (15.44)	15.91 (16.18)
[Ni(PBA) (H <sub>2</sub> O)]	50	296	D	50.13 (50.86)	3.08 (3.29)	12.93 (13.19)	13.16 (13.82)
[Ni(PDM) (H <sub>2</sub> O)]	45	254	D	55.98 (56.71)	2.86 (3.29)	11.12 (11.50)	11.78 (12.06)
[Pd(PAA) (H <sub>2</sub> O)]	60	350d	D	38.23 (38.80)	2.56 (2.98)	13.12 (13.65)	
[Pd(PBA) (H <sub>2</sub> O)]	70	285d	D	44.86 (45.33)	2.69 (2.95)	11.33 (11.85)	
[Pd(PDM) (H <sub>2</sub> O)]	75	220d	D	51.06 (51.45)	2.45 (2.98)	9.97 (10.48)	
[Fe(PAA) (OH) (H <sub>2</sub> O) <sub>2</sub> ]	62	a	5.91	39.76 (40.33)	3.78 (3.88)	13.86 (14.18)	14.00 (14.14)
[Fe(PBA) (OH) (H <sub>2</sub> O) <sub>2</sub> ]	58	a	5.93	47.88 (48.12)	3.69 (3.79)	12.15 (12.25)	12.16 (12.22)
[Fe(PDM) (OH) (H <sub>2</sub> O) <sub>2</sub> ]	56	a	5.94	53.69 (54.03)	3.58 (3.72)	10.58 (10.79)	10.83 (10.96)

a = does not melt or decompose below 350°C; d = decomposes; D = diamagnetic.

strong bands at  $\sim 1660 \text{ cm}^{-1}$  for free benzoyl carbonyl. Spectra of all the three ligands showed strong bands at  $\sim 1650 \text{ cm}^{-1}$  for the amide carbonyl of the phthalhydrazide moiety, and strong and broad bands at  $\sim 1615 \text{ cm}^{-1}$  for the internally hydrogen-bonded carbonyl of the  $\beta$ -diketone moiety.

In the spectra of the metal complexes, the latter band almost disappeared, but instead, another strong band, assignable to the stretching of the coordinated carbonyl of the  $\beta$ -diketone moiety appeared at  $\sim 1550 \text{ cm}^{-1}$  (Nakamoto 1978; Thankarajan and Krishnankutty 1984). A weak band observed at  $\sim 1620 \text{ cm}^{-1}$  in the spectra of the metal complexes is probably due to  $\nu_{\text{C}=\text{N}}$ , which might have been masked by the stronger carbonyl bands in the spectra of the ligands. A very broad band of the ligand at  $3500\text{--}2400 \text{ cm}^{-1}$ , due presumably to hydrogen-bonded OH/NH stretching, is replaced in the spectra of the metal complexes by a weaker broad band at  $3550\text{--}3350 \text{ cm}^{-1}$ , attributable to the amide N-H, and coordinated water. In the case of iron(III) complexes, their coordinated OH groups caused strong absorption and peak formation at  $\sim 3570 \text{ cm}^{-1}$ , in addition to a band at  $\sim 1130 \text{ cm}^{-1}$  for Fe-OH bonding (Nakamoto 1978).

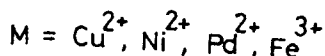
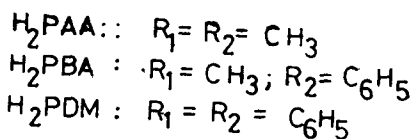
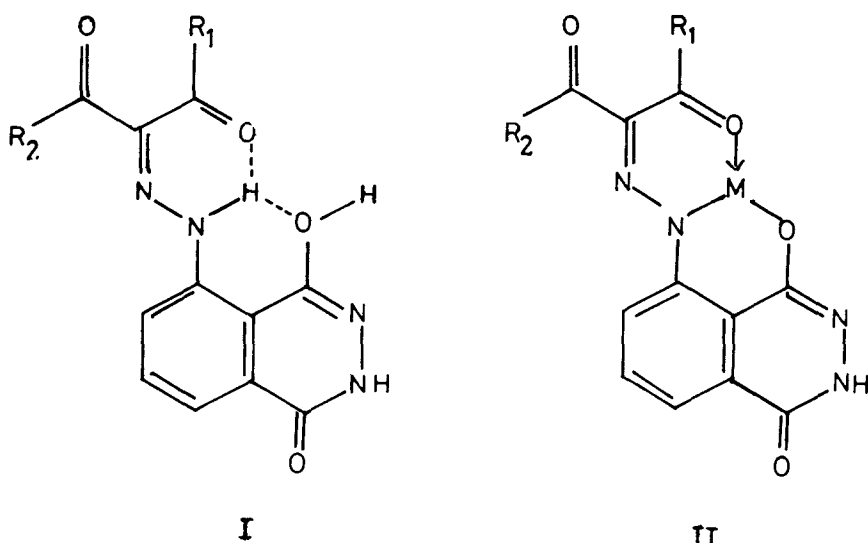


Chart 1.

### 3.2 $^1H$ NMR spectra of palladium(II) complexes

Further evidence for the bonding mode of the ligands (structure II) is provided by the  $^1H$  NMR spectra of their palladium(II) complexes. The non-equivalence of the two methyl protons (2.30 and 2.65 $\delta$ ) of  $H_2PAA$  (Thankarajan *et al* 1986) persists in its complex, (2.35 and 2.72 $\delta$ ). A low field broad one-proton signal at  $\sim 14\delta$  in the spectra of all the three ligands for hydrogen-bonded NH disappeared in the spectra of the complexes, indicating replacement of the NH proton during metal chelation. A comparatively broad one-proton signal at  $\sim 5.4\delta$  for the amide proton of the phthalhydrazide ring is present in the spectra of the ligands and of the metal complexes. The signal for the OH proton of the ligands could not be located in their spectra, presumably due to fast exchange.

### 3.3 Stability of copper(II) complexes

Order of stability on the basis of polarographic reduction potentials (table 2) of the three copper(II) complexes is  $-[Cu(PAA)(H_2O)] > [Cu(PBA)(H_2O)] > [Cu(PDM)(H_2O)]$ . Cross conjugation by pendant group(s) seems responsible for the destabilisation of metal chelates of  $H_2PBA$  and  $H_2PDA$ . Data for  $\nu(Cu-N)$  and  $\nu(Cu-O)$  from far IR spectra of the complexes (table 2) are in agreement with the stability order.

**Table 2.** Half-wave potentials and far IR data of copper(II) complexes.

Complex	$E_{1/2}$ (V) First wave	$\nu_{\text{Cu-N}}$ ( $\text{cm}^{-1}$ )	$\nu_{\text{Cu-O}}$ ( $\text{cm}^{-1}$ )	
[Cu(PAA) (H <sub>2</sub> O)]	-0.380	560	460	425 360
[Cu(PBA) (H <sub>2</sub> O)]	-0.365	548	453	418 368
[Cu(PDM) (H <sub>2</sub> O)]	-0.350	535	450	415 370

**Table 3.** Mössbauer spectral data of iron(III) complexes.

Complex	$\delta$ (mm/s)	$\Delta E_Q$ (mm/s)
[Fe(PAA) (OH) (H <sub>2</sub> O) <sub>2</sub> ]	+0.331	0.963
[Fe(PBA) (OH) (H <sub>2</sub> O) <sub>2</sub> ]	+0.368	0.959
[Fe(PDM) (OH) (H <sub>2</sub> O) <sub>2</sub> ]	+0.389	0.955

### 3.4 Mössbauer spectra of iron(III) complexes

Effect of cross resonance by pendant group on *d* electron delocalisation with the metal chelate ring was examined from Mössbauer spectral data of the iron(III) complexes. It is evident from observed  $\delta$  values (table 3) that *d* electron delocalisation with the chelate ring decreases when the pendant groups of chelate ring are changed from acetyl to benzoyl, and methyl to phenyl. Thus, it is evident that any cross conjugation of the metal chelate ring is not conducive to *d* electron delocalisation with the ring. Observed  $\Delta E_Q$  values reveal that increased *d* electron delocalisation with the chelate ring increases the field gradient at the nucleus.

### References

- Nakamoto K 1978 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: Wiley)
- Price R 1970 *The chemistry of synthetic dyes* (ed.) Venkataraman K (New York: Academic Press) vol. 3, p. 303
- Thankarajan N, Krishnankutty K and Srinivasan T K K 1986 *J. Indian Chem. Soc.* (in press)
- Thankarajan N and Krishnankutty K 1984 *Indian J. Chem.* A23 401
- Venkataraman K 1952 *The chemistry of synthetic dyes* (New York: Academic Press) vol. 1