

Studies on Complexes of Cu(II), Ni(II), Co(II) and Ln(III) with 3-(α -Benzoyl) Benzylidenehydrazino-5,6-Diphenyl-1,2,4-Triazine

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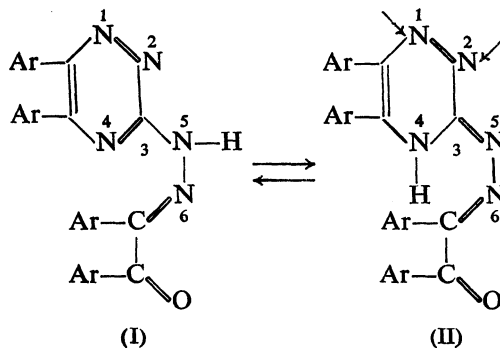
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The synthesis, acid-base equilibria and metal-ion chelating tendencies of 3-(α -benzoyl) benzylidenehydrazino-5,6-diphenyl-1,2,4-triazine (BHT) are reported. From potentiometric equilibrium measurements of hydrogen-ion concentration at 30°C and ionic strength 0.10 M KNO₃ in 75% (v/v) dioxane-water medium, the values of the stability constants of BHT with transition and lanthanide(III) ions have been evaluated. Probable structures of metal chelates are inferred from electronic absorption spectra and infrared examination of solid complexes. The use of BHT as analytical reagent for the spectrophotometric determination of copper, nickel and cobalt has also been discussed.

INTRODUCTION

1,2,4-Triazines¹⁻⁵ are well-known compounds and a wide variety of synthetic methods for the preparation of substituted derivatives are available. Compounds containing 1,2,4-triazine moiety are found in natural materials and some of these show biological activity⁶. Very recently 1,2,4-triazines have been shown to be intermediates for the synthesis of other nitrogen-containing heterocycles. Many 1,2,4-triazines form complexes with metal ions and can be used for their determination⁷. In the present communication, the metal-binding characteristics of one representative ketonic hydrazones, viz. 3-(α -benzoyl) benzylidenehydrazino-5,6-diphenyl-1,2,4-triazine (BHT) (I), is described.



EXPERIMENTAL

Preparation of the Solid Ligand and its Complexes

BHT was prepared as described in an earlier publication⁸. Copper, nickel and cobalt chelates were prepared by adding a dioxane solution of the ligand (0.025 mole) to an aqueous solution of metal nitrate (0.0125 mole). The pH of the solution was then increased to 3.5–4.0 and the mixture was refluxed for 1 hr. The reddish (in case of copper and nickel) and reddish brown precipitate obtained were filtered off, washed several times by aqueous dioxane and dried under vacuum. The analysis of the species prepared is shown in Table 1. It should be mentioned that the metal content was obtained through the decomposition of the solid by repeated treatment with concentrated nitric acid, then titrated against standard EDTA solution using suitable indicator.

TABLE 1
ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA FOR
METAL(II)-BHT COMPLEXES

Species and Formula	Calculated (Found)				Conductance* (ohm ⁻¹ cm ² mole ⁻¹)
	% C	% H	% N	% M	
BHT:					
C ₂₉ H ₂₁ N ₅ O	76.48 (76.28)	4.62 (4.72)	15.39 (15.55)		
Cu(BHT) ₂ :					
Cu[(C ₂₉ H ₂₀ N ₅ O) ₂]	71.64 (71.41)	4.12 (4.15)	14.41 (14.53)	6.54 (6.31)	13.2
Ni(BHT) ₂ :					
Ni[(C ₂₉ H ₂₀ N ₅ O) ₂ ·(H ₂ O) ₂]	69.41 (69.68)	4.39 (4.37)	13.96 (13.81)	5.86 (5.76)	7.35
Co(BHT) ₂ :					
Co[(C ₂₉ H ₂₀ N ₅ O) ₂ ·(H ₂ O) ₂]	69.40 (69.65)	4.39 (4.34)	13.96 (13.79)	5.98 (5.74)	6.51

*10⁻³ M complex in DMF.

Potentiometric titrations and experimental conditions are essentially the same as described earlier⁹.

Infrared spectra (potassium bromide discs) were recorded on a Perkin-Elmer 437 spectrometer (4000–300 cm⁻¹). The electronic spectra were measured at 25°C with Perkin-Elmer spectrometer 552, with 1 cm matched quartz cells.

The conductance of 1 × 10⁻³ M solution of the solid complex in purified DMF was measured using WTW, D-812 Weilheum conductivity meter, Model LBR, fitted with cell model LTA 100.

RESULTS AND DISCUSSION

Potentiometric Results

The pH-titration curves for free and complexed BHT are shown in Fig. 1a. Between $a = 0$ and $a = 1$, and in the presence of different metal ions, only one proton dissociates ($a = \text{moles of base added per mole of}$

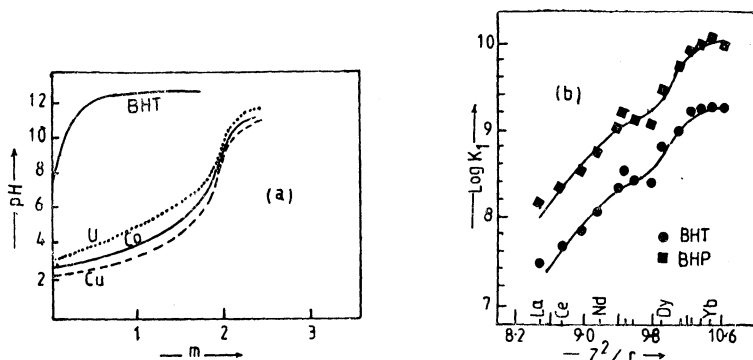


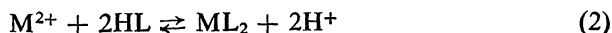
Fig. 1 (a) Potentiometric curves of BHT and its complexes with Cu(II), Co(II) and UO₂(II) ions at 30°C in 75% (v/v) dioxan-water solvent. [BHT] = 0.002M; [M₀] = 0.001M; $m = \text{moles of base added per mole of metal ion}$.

(b) Plots of $\log K_1$ for various lanthanide-BHT and lanthanide-BHP complexes as a function of ionic potential Z^2/r .

ligand present). This suggests that under these conditions the ligand behaves as monoprotic species, with the dissociation of the hydrazo proton. The acid dissociation constant, K^H , was calculated by using the relationship:

$$\log K^H = \log \frac{aC_L - [H^+] + [OH^-]}{(1-a)C_L + [H^+] - [OH^-]} + \text{pH} \quad (1)$$

Since the ionic product¹⁰, pK_w , of water in 75% (v/v) dioxane-water is approximately 18.7, both the hydrogen-ion and hydroxyl-ion concentration terms in Eq. (1) are negligible in the region of proton dissociation. The correction for pH values¹¹ in 75% (v/v) dioxane-water was taken as 0.28. The value of the pK^H calculated is given in Table 2. The titrate-curves obtained in the presence of bivalent cations showed an inflection at $m = 2$ (where $m = \text{moles of base added per mole of metal}$), corresponding to the formation of the bis-chelates, represented by the equilibrium:



As is clear from Fig. 1a the original pH value of the titration curves of Cu(II), Ni(II) and Co(II) is 2.2–2.3. This indicates that the equilibrium

is displaced almost completely towards the chelate giving a curve similar to that of a strong acid titration. The formation of Cu(II), Ni(II) and Co(II) chelates is clearly complete even at low pH, and correspondingly, their stabilities cannot be accurately calculated from potentiometric data.

For the lanthanide(III) or UO₂(II) ion complexes with BHT values of log K_n (n = 1 or 2) are calculated with the help of expression given by Irving and Rossotti¹²:

$$\log \frac{\bar{n}}{(n - \bar{n})} = \log K_1 + pL \quad (3)$$

$$\log \frac{(\bar{n} - 1)}{(2 - \bar{n})} = \log K_2 + pL \quad (4)$$

These expressions are solved by the graphic relation in the plot of log $\bar{n}/(1 - \bar{n})$ vs. pL or log $(\bar{n} - 1)/(2 - \bar{n})$ vs. pL; this gives straight line whose intercept with pL axis is taken as log K₁ or log K₂. These values are refined using the method of least square. The log of the formation constants of lanthanide ions with BHT are presented in Table 2. Values of log K₂ for the bis chelates of lanthanide ions with BHT are not included because of the tendency of these species to hydrolyse in the region of its formation.

TABLE 2
FORMATION CONSTANTS FOR BHT COMPLEXES WITH DIVALENT AND TRIVALENT METAL IONS
(t = 30°C; μ = 0.10; 75% (v/v) dioxane-water)

Cation	log K ₁ *	Cation	log K ₁
H ⁺	12.92	Dy ³⁺	8.82
La ³⁺	7.65	Ho ³⁺	9.09
Pr ³⁺	7.82	Er ³⁺	9.29
Nd ³⁺	8.03	Tm ³⁺	9.28
Sm ³⁺	8.35	Yb ³⁺	9.26
Eu ³⁺	8.55	Lu ³⁺	9.28
Gd ³⁺	8.44	UO ₂ ²⁺	11.97 log K ₂ † 9.62
Tb ³⁺	8.38		

* ± (0.01-0.02)

† ± 0.06

Spectral Results

The electronic absorption spectrum of the free ligand (75% dioxane-water mixture) displays three absorption bands with λ_{\max} at 230, 245 and 315 nm and molar absorptivities of 6.30×10^4 , 6.35×10^4 and 6.50×10^4 l.mole⁻¹ cm⁻¹ respectively, like those reported for triazine ring and its derivatives^{13,14}. The first band is due to $\pi-\pi^*$ transition of the benzenoid system of the compound. The second and third bands are attributed to enhanced $\pi-\pi^*$ transition (K-band) over the whole conjugate system and enhanced $n-\pi^*$ transition (R-band) respectively. The visible spectrum of the ligand in alkaline medium consists of one band with λ_{\max} at 395 nm representing the absorption of the ionic form, with decreasing pH, the absorbance of the band decreases while a new band is developed at shorter wavelength, *viz.*, 300 nm, representing the absorption of the non-ionic form.

An isosbestic point is observed denoting the existence of acid-base equilibrium of the type



The absorbance-pH plots are typical association or dissociation curves supporting the presence of acid-base equilibrium. The results were analyzed for the calculation of the dissociation constant (K^H) of the ligand in 75% (v/v) dioxane-water using the following equation:

$$A = A_L - \frac{[H^+](A - A_{HL})}{K^H} \quad (6)$$

where A , A_L and A_{HL} stand for the absorption of the mixture, anionic and neutral ligand species respectively. The value of $\log K^H$ obtained was found to be 13.00 ± 0.07 compared to 12.93 ± 0.03 as obtained potentiometrically.

In the visible region, the spectra of copper, nickel and cobalt complexes displayed an additional band as shown in Fig. 2b. The intensities of the peaks observed are function of both the pH of the medium (Fig. 2a) and the molar ratio of metal to ligand. The stoichiometry of the complexes were studied by applying the molar ratio method. The results proved that copper(II), nickel(II) and cobalt(II) form two types of complexes with stoichiometric ratio 1 : 1 and 1 : 2 metal to ligand (Fig. 3a).

Analytical Studies

BHT was used as a reagent for the determination of copper, nickel and cobalt spectrophotometrically. The colour is stable for more than 24 hrs and reaches maximum intensity within 5 min of mixing. The optimum pH is 3.5 for copper and nickel and 5.0 for cobalt. The systems obey Beer's law in the metal concentration range:

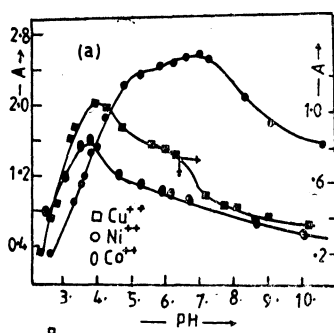
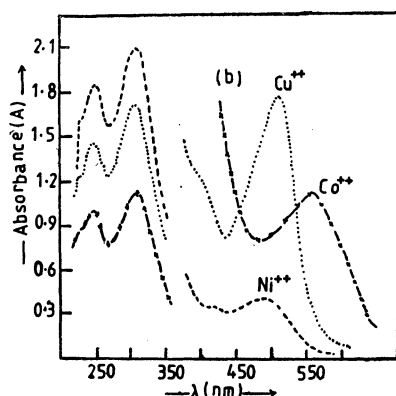


Fig. 2 (a) Absorption-pH plots for Cu(II)-BHT, Ni(II)-BHT and Co(II)-BHT species.



(b) Electronic absorption spectra of Cu(II)-BHT, Ni(II)-BHT and Co(II)-BHT chelates in 75% (v/v) dioxan-water BHT at optimum pH values.

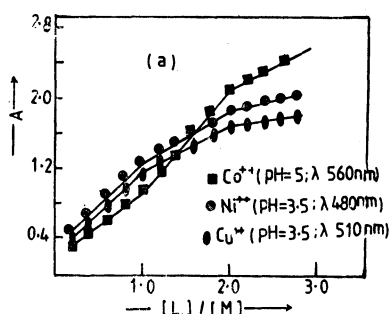
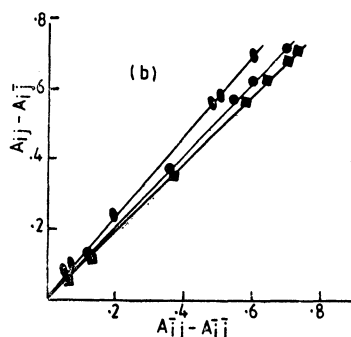


Fig. 3 (a) Molar ratio method for M(II)-BHT complexes at optimum pH values.



(b) Coleman plots for Ni(II)-BHT chelates.

copper: $3 \times 10^{-5} - 1 \times 10^{-4}$ M;
mole⁻¹ cm⁻¹,

nickel: $2 \times 10^{-5} - 2.2 \times 10^{-4}$ M;
mole⁻¹ cm⁻¹,

cobalt: $4.0 \times 10^{-5} - 2.0 \times 10^{-4}$ M;
mole⁻¹ cm⁻¹.

ϵ at λ_{\max} 510 nm = 1.75×10^4 l

ϵ at λ_{\max} 487.5 nm = 7.9×10^3 l

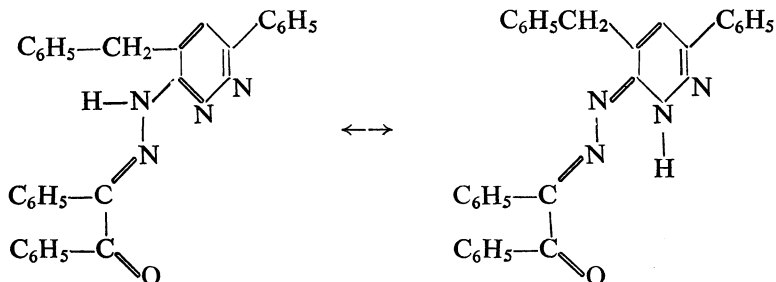
ϵ at λ_{\max} 560 nm = 6.94×10^3 l

Under optimum conditions, the relative deviation of the absorbance was 1.6% for copper, 1.4% for cobalt and 0.6% for nickel.

Protonation Equilibria

Comparison of the pK^H values of BHT (12.93) with those obtained for BHP (13.72)¹⁵, under similar experimental conditions reflects, at least partially, the differences in the basicity of NH group in both compounds. The difference to be 0.70 log unit between BHP and BHT. The

lower basicity of BHT could be attributed to the extent of conjugation in triazine ring more than pyridazine nucleus. This assignment is gained from results of IR spectra. The ν_{NH} appears as broad band at 3220–3250 cm^{-1} in the spectra of BHP¹⁵, while this band is noticed at 3300 cm^{-1} as a sharp intense band in BHT



Benzilmonohydrazone-3-hydrazino-4-benzyl-6-phenylpyridazine (BHP)

Complexation Studies

For purely electrostatic interaction, the strength of the bond expected to increase linearly with increasing the ionic potential Z^2/r where Z is the cationic charge and r is the ionic radius. Instead of the expected linearity, a curve is obtained, with a gradual increase in stability between lanthanum and europium followed by a plateau in the region gadolinium-terbium, and slight increase for the earlier heavy lanthanides, levelling in the thulium-lutetium region (Fig. 1b). This deviation beyond gadolinium has been attributed to change in hydration along the cationic series^{16,17}. The trend of the formation constants of Ln-BHT complexes reported here are much the same as reported previously for BHP¹⁵ ligand (Fig. 1b). The major differences between both systems are related to the difference in the basicities $\Sigma \text{pK}^{\text{H}}$ of the two ligands, which could result from the difference between triazine and pyridazine heterocyclic rings. The stabilities of complexes of the same type (ML) formed between a similar pair of ligands HT and HP (HT=BHT and HP=BHP) with lanthanide series are compared by plotting $\log K_{\text{MT}}^{\text{M}}$ vs. $\log K_{\text{MP}}^{\text{M}}$. This relation gives straight line of intercept equal to 0.70 and this indicates the validity of the equation

$$\log K_{\text{MP}}^{\text{M}} = \log K_{\text{MT}}^{\text{M}} + (\log K_{\text{HP}}^{\text{H}} - \log K_{\text{HT}}^{\text{H}}) \quad (9)$$

derived by Irving and Rossotti¹⁸. A conclusion could be drawn from this finding that BHT behaves as bidentate in a similar way to BHP, using one nitrogen of the grouping $-\text{NH}-\text{N}=\text{C}-$ and ketonic oxygen as coordination sites. In order to confirm this, the solid complexes were prepared. The results of elemental analysis and the values of the molar

conductance are given in Table 1. The values of the molar conductances in DMF indicated non-electrolytic nature of the complexes.

BHT is monobasic ligand with structure of different tautomeric forms among which are structures I and II. Two bands were noticed in the IR spectra of the ligand at 3300 and 1640 cm^{-1} could be assigned to ν_{NH} and $\nu_{\text{C=O}}$ respectively. These two bands show simultaneous disappearance in the IR spectra of the solid complexes (Table 4) indicating the participation of these groups in coordination.

TABLE 3
ABSORPTION SPECTRA OF BHT AND ITS METAL
COMPLEX IN 75% (v/v) DIOXANE-WATER

Species	max nm	log ϵ	Assignment
H(BHT)	230	4.70	$\pi - \pi^*$ Benzenoid
	245	4.70	$\pi - \pi^*$ (K-band)
	315	4.83	$n - \pi^*$ (R-band)
Cu-BHT	222.5	4.08	$\pi - \pi^*$ Benzenoid
	244.5	4.15	$\pi - \pi^*$ (K-band)
	305	4.24	$n - \pi^*$ (R-band)
	385- 405sh	4.07- 4.03	$d - \pi$
	510		$\pi - d$
Ni-BHT	222.5	4.50	$\pi - \pi^*$ Benzenoid
	240	4.56	$\pi - \pi^*$ (K-band)
	305	4.61	$n - \pi^*$ (R-band)
	400- 415sh	3.81- 3.84	$d - \pi$
	487.5	3.90	$\pi - d$
Co-BHT	222.5	3.69	$\pi - \pi^*$ Benzenoid
	240.5	3.79	$\pi - \pi^*$ (K-band)
	305	3.84	$n - \pi^*$ (R-band)
	465- 485sh		$d - \pi$
	560	3.84	$\pi - d$

The electronic spectra of solid Cu(II) complex were studied in DMF. The spectra show one broad band (550-590 nm) with λ_{max} at 580 nm and $\epsilon = 1.9 \times 10^4 \text{ l.mole}^{-1}.\text{cm}^{-1}$. The band can be assigned to ${}^2E_g \rightarrow {}^2T_{2g}$

transition. The position of λ_{\max} and the shape of the band indicate a square planar geometry for Cu(II)-BHT complex.

The ultraviolet spectra of Cu(II), Ni(II) and Co(II) complexes (Table 3) show the presence of two bands with λ_{\max} at 240–242.5 and 305 nm. These two bands are corresponding to the complexing agent. Also the spectra show the presence of a shoulder at 385–405 nm. The molar absorptivities of the bands are around 6.45×10^3 – 1.18×10^4 l.mole⁻¹ cm⁻¹ implying allowed electron transitions. The other bands (487.5–560 nm)

TABLE 4
SELECTED BAND GROUPS IN IR SPECTRA AND
THEIR TENTATIVE ASSIGNMENTS, (cm⁻¹)

Assignment	BHT	Cu-BHT	Ni-BHT	Co-BHT
ν_{HOH}	—	—	3440sb	3450sb
ν_{NH}	3300s	—	—	—
$\nu_{\text{C=O}}$	1640s	—	—	—
$\nu_{\text{C=C}}$; $\nu_{\text{C=N}}$	1590m	1590w	1590s	1590s
	1545w	1550w	1550w	1550w
$\nu_{\text{C-N(4)}}$ structure(II)*	1350s	—	—	—
$\nu_{\text{C-N(1)}}$ structure(II)*	1320s	1280w	1280w	1280w
$\nu_{\text{C-N(5)}}$ structure(I)*	1250m	—	—	—

*The atoms are numbered in the structures.

are relatively broad indicating high oscillator strength and are therefore perhaps charge-transfer in origin¹⁹. The band at lower frequency due to M → L transitions and that at higher frequency due to L → M transitions.

As is clear from Fig. 2a, with the increase of the pH of the medium the absorbance increases gradually till it attains a maximum, then decreases. The pH at which the maximum complex formation occurs are 3.5 for copper and nickel and 5.0 for cobalt. In cases of nickel and cobalt a buffer region is noticed at 4.5–6.0 and 5.0–7.0 respectively, after which the absorbance decreases with the pH increase. The decrease of the absorbance beyond the maximum is attributed to the hydrolysis of the complex to hydroxy derivatives as the OH⁻ ion concentration increases. This behaviour refers to the probable existence of more than one complex species in solution. The isobestic point noticed in the spectrum of Cu(II)-BHT in the pH region 3.85–6.20 indicates the existence of two absorbing species at least. The number of species in solution were determined applying Coleman²⁰ graphical method to the different data of BHT

complexes at several wavelengths and different relevant of pH values. The analysis revealed that only one absorbing species (MHL) in acidic region (2.25–3.25) and two absorbing species in the pH region 3.5–8.0 for the different systems as indicated by the linear plots shown in Fig. 3b.

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