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THERMAL, SPECTRAL AND MAGNETIC STUDIES OF SOME FIRST ROW TRANSITION METAL COMPLEXES OF 2-PHENYL-4-QUINOLINECARBOXYLIC ACID

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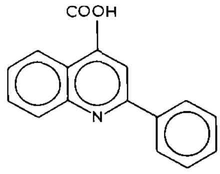
ABSTRACT

Some new compounds of 2-phenyl-4-quinolinecarboxylic acid with cobalt, nickel and copper were prepared. The thermal behaviour of these compounds together with that of the 2-phenyl-4-quinolinecarboxylic acid were studied by thermogravimetry and differential thermal analysis. The transition metal complexes are all hydrated. Thermal decomposition studies show that they lose water followed by organic ligand and halogen to give the metal oxide.

INTRODUCTION

The solid complexes obtained from the reaction between quinolines and transition metal ions have been studied in detail by a number of workers [1–5]. This work is a continuation and extension of the previous studies. The compound 2-phenyl-4-quinolinecarboxylic acid has two different donor sites: the oxygen atoms of the carboxylic acid groups and the nitrogen atom in the aromatic ring.



2-phenyl-4-quinolinecarboxylic acid (pqa)

This paper reports the thermal analysis studies of 2-phenyl-4-quinolinecarboxylic acid together with the complexes formed by the acid and the transition metals cobalt, nickel and copper. Spectral and magnetic studies

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were used to characterize each metal complex and to interpret the type of coordination to the metal ion. A study of the thermal stability of 2-phenyl-4-quinolinecarboxylic acid complexes was carried out.

EXPERIMENTAL

The compounds were prepared by the following method. 2-Phenyl-4-quinolinecarboxylic acid (0.02 mol) was dissolved in 220 cm^3 of warm ethanol. The metal halide (0.02 mol) was dissolved in 50 cm^3 of warm ethanol. The solutions were mixed and the volume was reduced until the complexes precipitated. The complexes were filtered, washed with warm ethanol and dried in a desiccator over calcium chloride.

The compounds prepared by this method are listed in Table 1. The analysis of the metal ion was determined using a Perkin–Elmer 373 atomic absorption spectrometer; the carbon, hydrogen and nitrogen analyses were carried out using a Carlo Erba elemental analyser. The electronic spectra. (Table 2) were obtained on a Beckman Acta MIV spectrophotometer as solid diffuse reflectance spectra. The IR spectra (Table 3) were obtained using KBr discs (4000–600 cm^{-1}) and polyethylene discs (600–200 cm^{-1}) on a Perkin–Elmer IR spectrophotometer, model 598. Magnetic measurements were carried out by the Gouy method using $Hg[Co(SCN)_4]$ as the calibrant. Each magnetic moment was corrected for diamagnetism using Pascal's constants [6]. The differential thermal analysis (DTA) studies were carried out on a Stanton Redcroft model STA 781 thermobalance. Thermogravimetric (TG) curves were obtained at a heating rate of 6 °C min^{-1} in static air. In all cases, a temperature range of 20–700 °C was studied.

RESULTS AND DISCUSSION

The compounds prepared (Table 1) have the stoichiometry $M(pqa)Cl_2 \cdot H_2O$ where M represents cobalt, nickel or copper.

The electronic spectra (Table 2) and the magnetic measurements (Table 1) suggest that for the cobalt and nickel compounds the metal ion is in an octahedral environment [7]. For the cobalt compounds the three spin-allowed transitions, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, are observed. For the nickel compounds only two of the spin-allowed transitions, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, are observed. The third transition, ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, is not observed due to the charge transfer band at 30120 cm^{-1} which extends into the visible region. The copper compound has a broad absorption band between 10000 and 15000 cm^{-1}. This suggests an octahedral environment for the copper atom [7] since square planar copper(II) compounds show bands of near equal intensity at

TABLE 1

Analyses and magnetic moments of compounds

Compounds	Colour	Theory (%)				Experimental (%)				μ_B
		M	C	H	N	M	C	H	N	
$Co(pqa)Cl_2 \cdot H_2O$	Violet	14.84	48.39	3.31	3.53	14.41	47.92	3.17	3.44	5.21
$Ni(pqa)Cl_2 \cdot H_2O$	Yellow	14.79	48.42	3.31	3.53	14.01	48.21	3.12	3.33	3.49
$Cu(pqa)Cl_2 \cdot H_2O$	Yellow	15.82	47.83	3.27	3.49	15.43	47.66	3.08	3.41	2.09

pqa = 2-phenyl-4-quinolinecarboxylic acid.

TABLE 2

Electronic spectra of the compounds (cm^{-1})

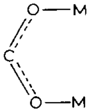
Compound	Band position	d–d transition
$Co(pqa)Cl_2 \cdot H_2O$	6623	$^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$
	15038	$^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$
	18868	$^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$
$Ni(pqa)Cl_2 \cdot H_2O$	6756	$^3A_{2g}(F) \rightarrow {}^3T_2g(F)$
	11933	$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$
	30120 (CT) [a]	
$Cu(pqa)Cl_2 \cdot H_2O$	12346	$^2E_g(D) \rightarrow {}^2T_{2g}(D)$

[a] CT, charge transfer.

about 15000–18000 cm^{-1} [9–11] and regular tetrahedral compounds have bands below 10000 cm^{-1} [12]. The magnetic moment for the copper compound is greater than the spin-only value indicating some orbital contribution.

In Table 3 the main bands in the IR spectra of the compounds are listed. The complexes show a strong broad absorption band in the region 3660–3140 cm^{-1} due to the ν_{O-H} vibration, indicating the presence of water of crystallization [7]. The complexes show an absorption band in the region 3130–3030 cm^{-1} which has been assigned to the ν_{N-H} vibration [12]. This band is absent in the spectrum of the free ligand. The compounds also show an absorption band around 1600 cm^{-1} due to the stretching vibration of the carboxylate groups linked to the metal ions. An increase in carboxylate resonance causes single bond character in the carbonyl group which is observed by a lowering of the frequency of the C=O stretching vibration [13]. It is suggested that bonding type (I) rather than (II) is observed [14].

(I)



(II)

The assignment of the bands due to the ring vibrations of the quinoline ring system in the complexes is similar to that for the free ligand indicating

TABLE 3

IR spectrum (4000–200 cm^{-1})

Compound	$\nu_{O-H}(H_2O)$	ν_{N-H}	ν_{COOH}	ν_{COO^-}	ν_{C-O}	ν_{M-Cl}	ν_{M-O}
pqa			1700(s)		1442(s)		
$Co(pqa)Cl_2 \cdot H_2O$	3660–3140 (br,s)	3082(m)		1606(s)	1422(s)	232(w)	272(m)
$Ni(pqa)Cl_2 \cdot H_2O$	3660–3142 (br,s)	3080(m)		1607(s)	1423(s)	206(w)	282(m)
$Cu(pqa)Cl_2 \cdot H_2O$	3660–3158 (br,s)	3070(m)		1585(s)	1429(s)	210(w)	298(m)

s, strong; br, broad; m, medium; w, weak.

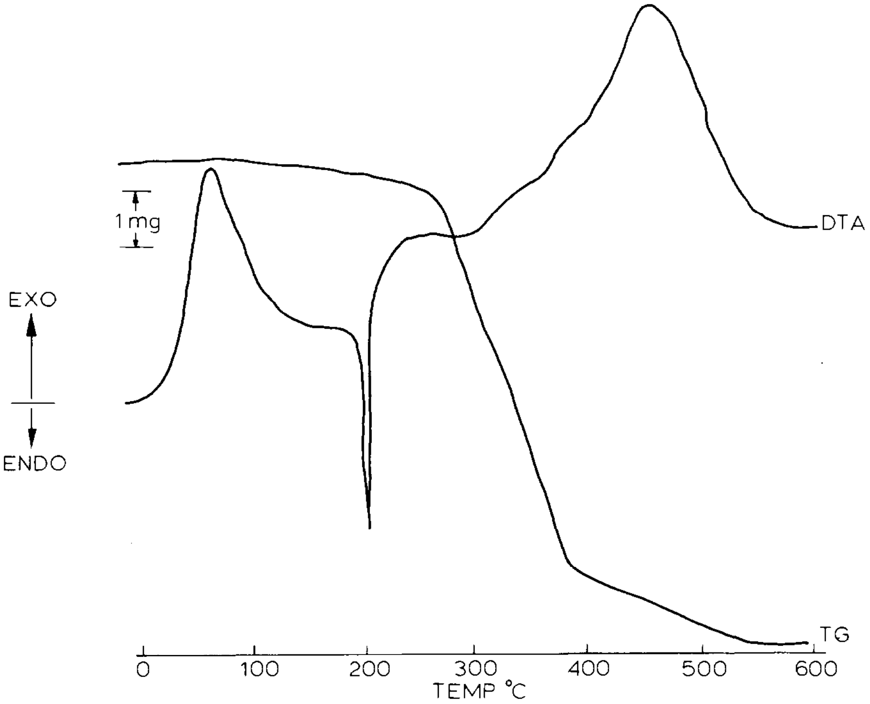


Fig. 1. TG and DTA curves for 2-phenyl-4-quinolinecarboxylic acid (sample weight = 8.89 mg).

the absence of metal–nitrogen bonding in these compounds [7]. The assignment of the bands due to the metal–oxygen vibrations indicate a six-coordinate environment for the metal ions [15]. The position of the bands due to the metal–halogen vibrations suggest the presence of bridging halogen atoms in these compounds [7].

The insolubility of the compounds in both polar and non-polar solvents is indicative of a polymeric structure [7].

The fact that the compounds were isolated as powders and not as single crystals meant that no complete structure determination could be made. However, spectroscopic and magnetic data enable us to predict that the metal ions are in an octahedral environment in the compounds. It is thus postulated that the structure of the compounds is a chain of metal atoms bonded to halogens with the carboxylate ion of the 2-phenyl-4-quinolinecarboxylic acid coordinating to give a six-coordinate environment for the metal ions. It is further suggested that the water molecules are attached to the structures by hydrogen bonding.

The TG and DTA diagrams for 2-phenyl-4-quinolinecarboxylic acid and its chloro complexes with cobalt(II), nickel(II) and copper(II) are shown in Figs. 1–4. The TG and DTA curves for 2-phenyl-4-quinolinecarboxylic acid (Fig. 1) show that the compound immediately undergoes an exothermic

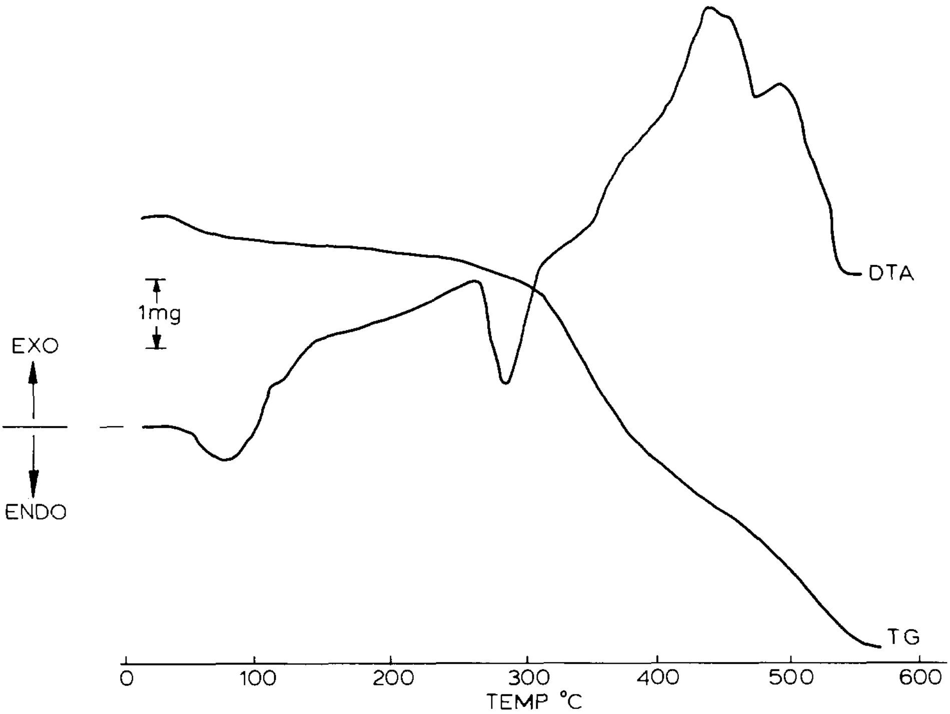


Fig. 2. TG and DTA curves for $Co(pqa)Cl_2 \cdot H_2O$ (sample weight = 7.87 mg).

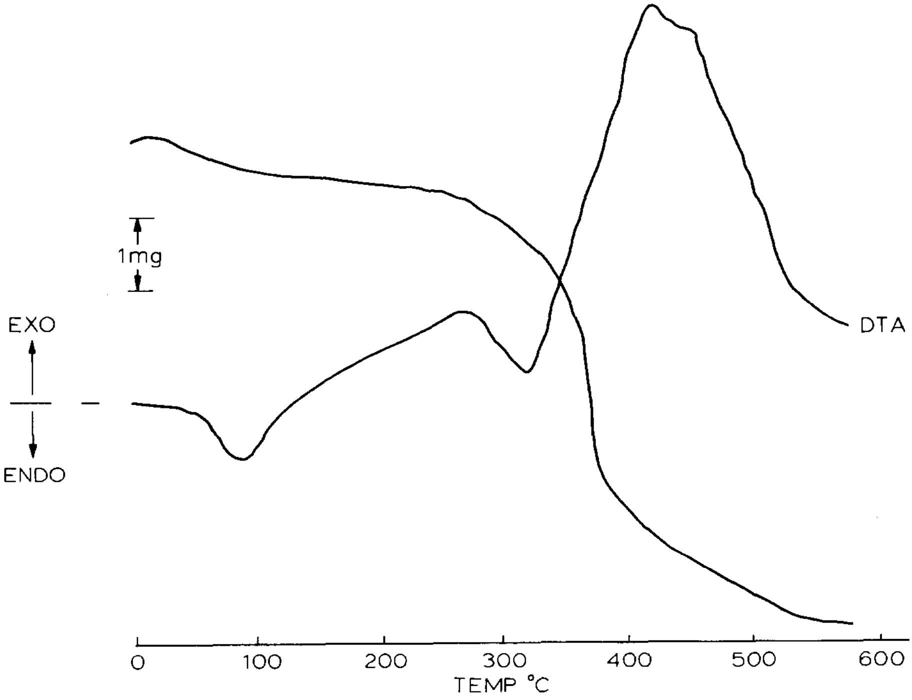


Fig. 3. TG and DTA curves for $Ni(pqa)Cl_2 \cdot H_2O$ (sample weight = 8.83 mg).

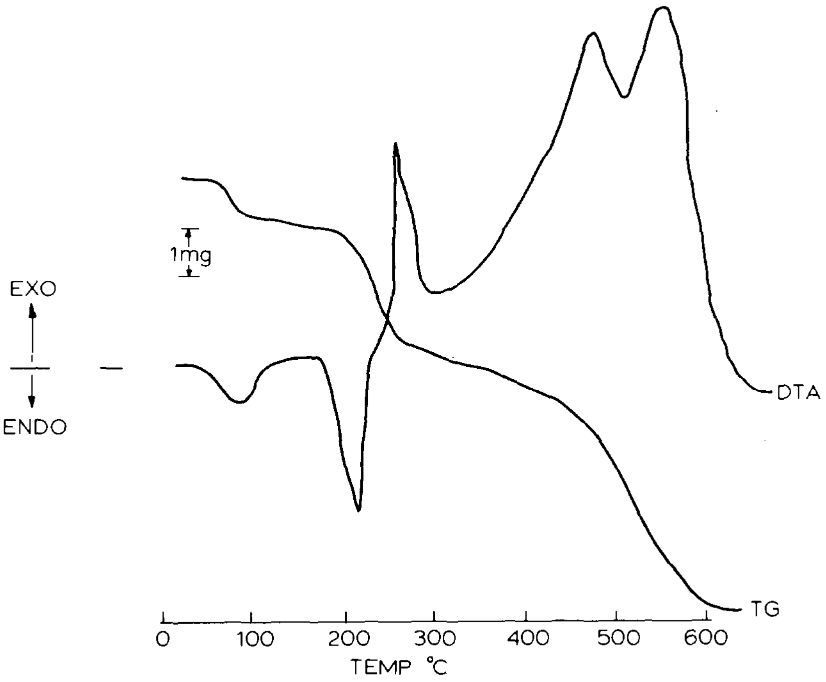


Fig. 4. TG and DTA curves for $Cu(pqa)Cl_2 \cdot H_2O$ (sample weight = 10.21 mg).

reaction. Its pyrolytic decomposition starts at 70 °C and finishes around 560 °C with total elimination of the sample. The DTA curve shows a peak at 215 °C corresponding to fusion. The value of the fusion enthalpy calculated from the area of this peak is 4.39 J g^{-1}. Liquid 2-phenyl-4-quinolinecarboxylic acid decomposes immediately with an exothermic band at 480 °C.

The TG and DTA curves for the 2-phenyl-4-quinolinecarboxylate complexes are shown in Figs. 2–4. The dehydration of the complexes starts below 100 °C suggesting that the water is present as water of crystallization [16]. The dehydration of the complexes takes place in one step. The observed weight losses for these processes compare favourably with the theoretical

TABLE 4

Dehydration processes of metal complexes

Process	Peak temp. (°C)	Thermal nature of transformation	Weight loss (%)		Enthalpy (kJ mol^{-1})
			Calc.	Found	
$Co(pqa)Cl_2 \cdot H_2O \rightarrow Co(pqa)Cl_2$	74.4	Endo	4.53	4.45	11.62
$Ni(pqa)Cl_2 \cdot H_2O \rightarrow Ni(pqa)Cl_2$	91.3	Endo	4.53	4.86	41.03
$Cu(pqa)Cl_2 \cdot H_2O \rightarrow Cu(pqa)Cl_2$	88.7	Endo	4.47	4.99	45.94

TABLE 5

Decomposition processes of 2-phenyl-4-quinolinecarboxylic acid and metal complexes

Process	Temp. range (°C)	Thermal nature of transformation	Residue (%)	
			Calc.	Found
pqa → pyrolytic process	70 → 560	Endo/exo	–	–
$Co(pqa)Cl_2 \rightarrow Co_3O_4$	118 → 562	Endo/exo	20.20	19.05
$Ni(pqa)Cl_2 \rightarrow NiO$	114 → 548	Endo/exo	18.81	19.25
$Cu(pqa)Cl_2 \rightarrow CuO$	178 → 607	Endo/exo	19.79	19.58

values (Table 4). The expected endothermic peak for the dehydration of these compounds is observed in their DTA curves. The dehydration enthalpies were calculated and are given in Table 4. The decomposition of the anhydrous complexes follows immediately after the dehydration and the residual weights are in good agreement with the values required for metallic oxides (Table 5). In the DTA curves the decomposition processes correspond to an endothermic reaction immediately followed by an exothermic reaction.

The stoichiometry of the residue of the pyrolytic decomposition of the metal complexes was established by metal analysis of the residues.

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