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Synthesis and spectral studies on Co(II) and Ni(II) complexes with polyfunctional quinazoline-(3H)-4-ones

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Abstract. A series of complexes of Co(II) and Ni(II) with 2-(R)-3-(X)-substituted quinazoline-(3H)-4-ones, where R = methyl/phenyl and X = furalamino, uramino and thiouramino have been synthesised and characterised by analytical, conductivity, thermal and magnetic, infrared and electronic spectral data. Based on analytical and conductivity studies the stoichiometries of the complexes have been established. Conductivity data also show that all these complexes are non-electrolytes. Infrared spectral data indicate that all the ligands manifest neutral bidentate with both the metal ions. Geometries for the complexes have been proposed based on electronic spectral data. Various electronic spectral parameters have been calculated for all the complexes and relevant conclusions have been drawn with respect to the nature of bonds present in them.

Keywords. Quinazolines; neutral bidentate ligands; electronic spectra; octahedral geometry; bivalent metal complexes.

1. Introduction

In continuation of our earlier work (Prabhakar *et al* 1988, 1989, 1990) we synthesized the complexes of Co(II) and Ni(II) with 2-(R)-3-(X)-substituted quinazoline-(3H)-4-ones, where R = methyl/phenyl, X = furalamino (MFQ/PFQ), uramino (MUQ/PUQ) and thiouramino (MTUQ/PTUQ) (figure 1). The complexes are characterized based on analytical, conductivity, thermal, magnetic and IR and electronic spectral data.

2. Materials and methods

2.1 *Materials*

All the chemicals used were of AR grade. The ligands were prepared by literature methods (Soliman 1973; Ravishankar 1984). The purity of these compounds were checked by TLC and melting point determinations.

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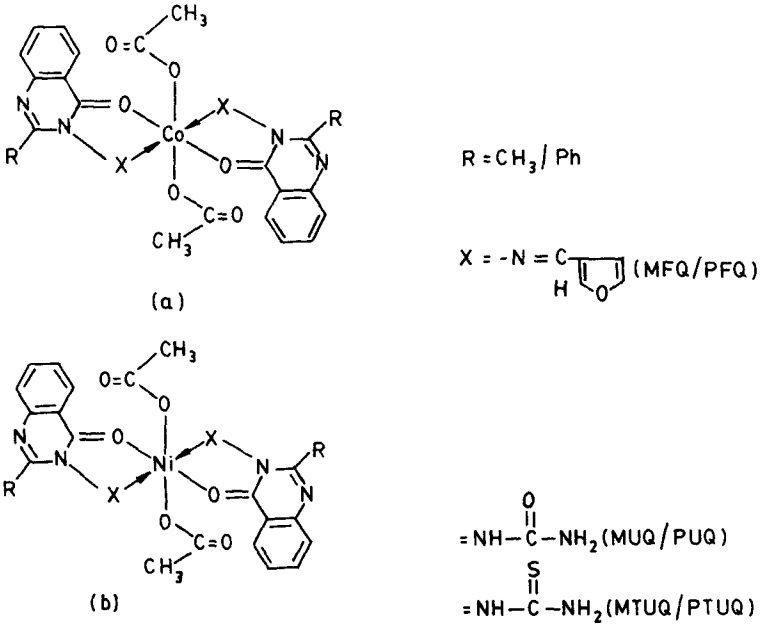

Figure 1. Structure of (**a**) Co(II) complexes; (**b**) Ni(II) complexes.

2.2 *Preparation of metal complexes*

In the preparation of the Co(II) and Ni(II) complexes the following general procedure was adopted. Metal acetate solution (1 m mol) in methanol was added dropwise to a solution of the ligand in methanol/acetone (3 m mol) with constant stirring. In all cases, the ligand concentration was in slight excess of the 1:3 (metal–ligand) molar ratio. The reaction mixture was refluxed on a water bath for 30–60 min. The complexes, which separated out on cooling, were filtered through a sintered glass crucible, washed several times with methanol and finally with acetone and then dried in vacuum over fused calcium chloride. The yields of the complexes are in the range 55–70%.

2.3 *Physical measurements*

Analytical data (C, H, N and S) for the ligands and their metal complexes were obtained from the Microanalytical Laboratory, Calcutta University, Calcutta. After heating to decomposition temperature the metal contents of the complexes were determined by using standard procedures (Vogel 1961). Molar conductivities of the complexes in DMF were measured using a Digisun Digital Conductivity Meter, Model DI-909. Thermal data of the complexes were obtained using a Stanton thermobalance available at the Indian Institute of Chemical Technology, Hyderabad. IR spectra of the ligands and their complexes (4000–200 cm^{-1}) in Nujol mulls and KBr pellets (using CsI plates in the far-IR region) were obtained using a Perkin Elmer-283 spectrometer. Magnetic measurements of the complexes in the solid state were made on a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were applied using Pascal's constants. The electronic spectra of the complexes in DMF were recorded on a Shimadzu MPS-5000 spectrometer.

3. Results and discussion

All the complexes are stable at room temperature, non-hygroscopic and insoluble in water and in many of the common organic solvents but are soluble in DMF and DMSO. The analytical and physical data of the complexes are listed in table 1. Analytical data of the complexes indicate that the metal–ligand molar ratio is 1:2 and all the complexes are also associated with two acetate ions. The molar conductance values of the complexes in DMF are in the range 5–18 mhos cm^2 mol^{-1}, indicating their non-electrolytic nature (Geary 1971).

3.1 *Thermal study*

Decomposition temperatures, determined from thermograms, are given in table 1. The complexes are thermally stable upto 200°C and are not hydrated. This is also confirmed by their DTA curves which do not exhibit an endothermic peak in the 100–200°C temperature range. The sharp decomposition associated with the loss of ligands starts above 230°C. The final decomposition products above 580°C in every case correspond to metallic oxide. The thermal stability of Co(II) complexes with various ligands is reflected in the following order: PFQ < MTUQ < MFQ ~ MUQ < PUQ < PTUQ. This order is commensurate with π-electron delocalization, the size of the molecule and also the number of rings formed (Nikoleeve *et al* 1969).

3.2 *Infrared spectra*

Important absorption frequencies of the ligands and their complexes, along with their assignments, are listed in table 2. A strong band corresponding to ν(C=O) at 1700 cm^{-1} of the quinazoline ring is shifted to lower wavenumbers by 40–50 cm^{-1} in the spectra of all the complexes, indicating that the carbonyl oxygen is invariably involved in coordination (Sahai *et al* 1982). The band at 1640 cm^{-1} due to ν(C=N) of the quinazoline ring remains unaltered in the spectra of complexes, whereas the band at 1600 cm^{-1} due to the furalamino group present in MFQ and PFQ undergoes a lower shift of 40–50 cm^{-1} suggesting coordination through this nitrogen (Prabhakaran and Patel 1972).

The ν(N–H) frequency observed at 3300 cm^{-1} in MUQ, PUQ, MTUQ and PTUQ is shifted to a lower region ($\Delta\nu = 50\,cm^{-1}$) in all the complexes, indicating the involvement of the imino nitrogen in coordination (Sengupta *et al* 1981). The bands due to $\nu(NH_2)$ (MUQ, PUQ, MTUQ and PTUQ) (Agarwal *et al* 1983) ν(C=O) (MUQ and PUQ) (Soliman *et al* 1979) and ν(C=S) (MTUQ and PTUQ) (Mukkanti *et al* 1988) at 3400, 1660 and 860 cm^{-1} respectively, remain unaltered in the complexes, indicating non-participation of the N/O/S of these groups in coordination. In addition, the IR spectra of the complexes show bands around 1510, 1450, 1340 and 710 cm^{-1} which can be assigned to $\nu_{as}(COO)$, $\nu_s(COO)$, $\delta(CH_3)$ and δ(OCO) vibrations respectively indicating the presence of acetate ions in the coordination spheres (Nakamato 1978). This mode of coordination is further supported by the appearance of ν(M–O) and ν(M–N) bands around 400 and 500 cm^{-1} respectively in their FIR region (Adams 1967; Behnke 1967).

Table 1. Analytical and physical data of the complexes.

Complex	Colour	Decomposition temperature (°C)[a]	Analysis (%)[b]					Molar conductance (mho cm^2 mol^{-1})	Yield (%)
			Metal	Carbon	Nitrogen	Hydrogen	Sulphur		
$[Co(MFQ)_2(CH_3COO)_2]$	Dark brown	315	8·60 (8·63)	56·20 (56·22)	12·26 (12·29)	4·05 (4·09)	—	5	60
$[Co(PFQ)_2(CH_3COO)_2]$	Green	305	7·27 (7·31)	62·40 (62·45)	10·38 (10·40)	3·92 (3·96)	—	8	55
$[Co(MUQ)_2(CH_3COO)_2]$	Light brown	315	9·58 (9·62)	46·90 (46·98)	18·22 (18·27)	4·22 (4·24)	—	8	58
$[Co(PUQ)_2(CH_3COO)_2]$	Blue	318	8·00 (8·00)	55·30 (55·35)	15·17 (15·19)	4·06 (4·07)	—	13	60
$[Co(MTUQ)_2(CH_3COO)_2]$	Snuff coloured	310	9·10 (9·14)	44·62 (44·65)	17·32 (17·36)	4·02 (4·03)	9·90 (9·92)	7	55
$[Co(PTUQ)_2(CH_3COO)_2]$	Dark brown	320	7·62 (7·67)	53·01 (53·05)	14·52 (14·56)	3·90 (3·90)	8·30 (8·32)	14	60
$[Ni(MFQ)_2(CH_3COO)_2]$	Light blue	318	8·58 (8·63)	56·18 (56·22)	12·12 (12·29)	4·02 (4·02)	—	14	70
$[Ni(PFQ)_2(CH_3COO)_2]$	Light blue	300	7·28 (7·31)	62·40 (62·45)	10·35 (10·40)	3·90 (3·92)	—	16	62
$[Ni(MUQ)_2(CH_3COO)_2]$	Light yellow	325	9·59 (9·62)	46·91 (46·98)	18·21 (18·27)	4·20 (4·24)	—	18	65
$[Ni(PUQ)_2(CH_3COO)_2]$	Blue	318	7·93 (8·00)	55·30 (55·35)	15·10 (15·12)	4·00 (4·07)	—	10	60
$[Ni(MTUQ)_2(CH_3COO)_2]$	Light brown	310	9·10 (9·14)	44·50 (44·65)	17·30 (17·36)	4·00 (4·03)	9·89 (9·92)	12	55
$[Ni(PTUQ)_2(CH_3COO)_2]$	Snuff coloured	328	7·61 (7·67)	53·00 (53·05)	14·51 (14·56)	3·87 (3·90)	8·30 (8·32)	11	55

[a]All the complexes decompose above the temperature cited; [b]values in parentheses are calculated

Table 2. Assignment of some important infrared spectral data of the complexes.

Complex	Infrared assignment (cm^{-1})[a]				
	ν(C=O) (quinazoline ring)	ν(NH)	ν(C=N) (furalamino)	ν(M–O)	ν(M–N)
$[Co(MFQ)_2(CH_3COO)_2]$	1650(1700)	—	1550(1600)	420,440	470
$[Co(PFQ)_2(CH_3COO)_2]$	1650(1700)	—	1560(1600)	420,450	490
$[Co(MUQ)_2(CH_3COO)_2]$	1640(1700)	3230(3300)	—	435,450	500
$[Co(PUQ)_2(CH_3COO)_2]$	1640(1700)	3260(3300)	—	400,440	490
$[Co(MTUQ)_2(CH_3COO)_2]$	1655(1690)	3280(3300)	—	410,440	480
$[Co(PTUQ)_2(CH_3COO)_2]$	1640(1700)	3270(3300)	—	400,450	500
$[Ni(MFQ)_2(CH_3COO)_2]$	1650(1700)	—	1550(1600)	400,450	500
$[Ni(PFQ)_2(CH_3COO)_2]$	1660(1700)	—	1550(1600)	390,420	490
$[Ni(MUQ)_2(CH_3COO)_2]$	1650(1700)	3220(3300)	—	410,430	500
$[Ni(PUQ)_2(CH_3COO)_2]$	1640(1700)	3250(3300)	—	420,440	480
$[Ni(MTUQ)_2(CH_3COO)_2]$	1640(1690)	3270(3300)	—	420,450	490
$[Ni(PTUQ)_2(CH_3COO)_2]$	1660(1700)	3260(3300)	—	400,440	500

[a]Values in parentheses are free ligand bands

3.3 *Electronic spectra*

Electronic spectral data of the complexes along with their assignments are presented in table 3.

The ligands exhibit strong bands around 34,000 and 31,000 cm^{-1} which may be assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively. Electronic spectra of Co(II) complexes display three bands around 8 350, 17,100 and 20,100 cm^{-1} which may be assigned to the spin-allowed transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) respectively, characteristic of octahedral geometry around Co(II) ion (Matthews and Walton 1971). Nickel (II) complexes also exhibit three bands in their electronic spectra around 9 300, 15,200 and 25,000 cm^{-1} and these have been respectively assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions characteristic of octahedral geometry (Sacconi 1968). The octahedral geometry of Co(II) and Ni(II) complexes is further supported by the ν_2/ν_1 ratios which lie around 2·09 and 1·67 respectively. The values of ν_2/ν_1 obtained for the complexes are lower than that of regular octahedral aquo complexes which may be due to the asymmetric environment around Co(II) and Ni(II).

Various ligand field parameters, such as the ligand field splitting energy ($10D_q$), Racah interelectronic repulsion parameter (B), covalent factor (β) and ligand field stabilization energy (LFSE) have been calculated for all the Co(II) and Ni(II) complexes (Lever 1968). The calculated $10D_q$ values of Co(II) and Ni(II) complexes suggest a position between water and ammonia in the spectrochemical series for these ligands. B values for the complexes are lower than the free ion values, thus indicating orbital overlap and delocalization of d-orbitals. The β-values obtained are less than one suggesting a considerable amount of covalent character in the metal-ligand bonds.

3.4 *Magnetic moments*

The experimental and calculated magnetic moments of the complexes are given in table 3.

Table 3. Magnetic moments and electronic spectral data and relevant ligand field parameters of the complexes.

Complex	$\nu_1(cm^{-1})$	$\nu_2(cm^{-1})$	$\nu_3(cm^{-1})$	ν_2/ν_1	$10D_q(cm^{-1})$	$B(cm^{-1})$	β	LFSE (k cal mol^{-1})	μ_{eff}(B.M)
$[Co(MFQ)_2(CH_3COO)_2]$	8250	16950	19900	2·06	8700	807	0·72	19·89	5·16 (5·20)
$[Co(PFQ)_2(CH_3COO)_2]$	8350	17100	20100	2·05	8750	810	0·72	20·00	5·03 (5·04)
$[Co(MUQ)_2(CH_3COO)_2]$	8000	16000	19500	2·00	8000	766	0·68	18·29	4·99 (5·01)
$[Co(PUQ)_2(CH_3COO)_2]$	8050	16800	19650	2·09	8750	820	0·72	20·00	5·04 (5·12)
$[Co(MTUQ)_2(CH_3COO)_2]$	8200	16100	19600	1·96	7900	740	0·65	18·05	4·98 (5·00)
$[Co(PTUQ)_2(CH_3COO)_2]$	8350	17100	20100	2·05	8750	810	0·72	20·00	4·99 (5·01)
$[Ni(MFQ)_2(CH_3COO)_2]$	8900	14800	25200	1·66	8900	887	0·85	30·51	3·18 (3·20)
$[Ni(PFQ)_2(CH_3COO)_2]$	9300	15200	24900	1·63	9300	813	0·78	31·89	3·18 (3·18)
$[Ni(MUQ)_2(CH_3COO)_2]$	9100	14850	25000	1·63	9100	837	0·80	31·20	3·28 (3·33)
$[Ni(PUQ)_2(CH_3COO)_2]$	8870	14730	25000	1·66	8870	881	0·85	30·40	3·26 (3·28)
$[Ni(MTUQ)_2(CH_3COO)_2]$	9050	15100	24000	1·67	6050	796	0·76	20·76	3·20 (3·26)
$[Ni(PTUQ)_2(CH_3CO)_2]$	9000	15000	24200	1·67	6000	813	0·76	20·57	3·18 (3·22)

[a]Values in parentheses are calculated

All the Co(II) and Ni(II) complexes are found to be paramagnetic and to have a magnetic moment corresponding to octahedral geometry (Figgis 1966; Khulbe *et al* 1981). μ_{eff} values have also been calculated using $10D_q$ and are in good agreement with experimental values suggesting considerable orbital contribution.

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