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Tetradentate Schiff Base Chelates of Copper(II) and Nickel(II): Halogenation and Phenylisocyanation

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Halogenation (chlorination, bromination and iodination) and phenyl isocyanation reactions are conducted on newly synthesised bis(polyamines acetylacetoneimine) of nickel(II) and copper(II).

Key Words: Schiff base, Diethylenetriamine, Nickel(II) and Copper(II) chelates, Phenylisocyanation.

INTRODUCTION

The γ(CH) electrophilic substitution reactions of β-ketoimines are in general much less investigated compared to the corresponding reactions of β-diketonates and β-ketoesters[1]. This may, probably, be due to the hydrolytic instability of the parent β-ketomine metal chelates. Again, almost these less explored γ(CH) substitution reactions of β-ketoiminates, the hetero groups process substitution reactions, at both the γ(CH) of the metal chelate rings (*i.e.*, γ(C—X/Y), where X ≠ Y ≠ H) have been less reported[2–11]. Though several chelates have heen well synthesized using tetradentate Schiff base chelates involving ethylenediamine and acetylacetone[12], tetradentate Schiff base chelates involving acetyl acetone and diethylenetriamine are not yet synthesized. Similarly, though the electrophilic substitution of transition metal complexes of monovalent β-diketones are quite well studied[13], the corresponding analogue reactions of bivalent and tetravalent metal β-ketominates are not known to many, although not quite unknown altogether. Earlier diazo coupling reactions of arene diazonium chlorides with metal β-ketoimine leading to the formation of mono and bis(glyoxalarylhydrazineimino) metal(II) complexes instead of arylazo substituted products[14, 15]. In addition to this, synthesis of crown ether dyes and their ion complexation properties have been reported[16]. Herein we first synthesize and the reactivity of bivalent quadridentate Schiff base metal(II) chelates derived from β-diketones and diethylenetriamine. A series of bivalent tetradentate schiff base Ni(II) and Cu(II) chelates are subjected to a variety of reactions like chlorination, bromination, iodination and phenyl isocyanation etc. The results of these reactions and their substitution products have been well discussed in terms of the analytical and spectral characterization of the end products.

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EXPERIMENTAL

Preparation of ligand[17, 18]**:** 0.01 mol of diethylenetriamine in ethanol was added to 0.02 mol of acetylacetone by stirring in an ice bath. The mixture was recrystallized from hot ethanol.

Preparation of the complex M(II) (badt): The ligand bis(acetylacetone-diethylenetriamine) (badt) (0.01 mol) was dissolved in water containing ethanol. This was made basic by adding NH_3. 0.01 mol of copper acetate in water containing ethanol was added to it and refluxed for 3 h. The precipitated complex was then filtered and recrystallized from an acetone solution. Purple colour crystals are obtained.

TABLE-1
ANALYTICAL DATA OF Cu(II) AND Ni(II) COMPLEXES

Complex	Analytical data %, found (calcd.)				m.p. (°C)	μ_{eff} (B.M.)
	C	H	N	M		
$C_{14}H_{23}N_3O_2Cu$	51.4 (51.13)	7.2 (7.0)	12.9 (12.7)	19.1 (19.3)	210–215	1.90
$C_{14}H_{23}N_3O_2Ni$	51.7 (51.9)	7.3 (7.1)	12.7 (12.9)	18.33 (18.13)	280–285	Diamagnetic

Halogenation of M(badt)[19, 20]**:** N-Bromosuccinimide, N-chlorosuccinimide are general halogenating agents which are used, replacing the ring hydrogen of metal β-dicarbonyl chelates with halogens. But iodination was conducted by using the iodinating agent monopyridiniodine(I) chloride.

Cu(II)(badt)Br$_2$: To 20 meq. of M(II) (badt) in 25 mL chloroform, 22 meq. of powdered N-bromosuccinimide was added with stirring. After 5 min, the reaction mixture was heated and concentrated to 10 mL in a stream of nitrogen. Approximately 50–100 mL of petroleum ether was added and the precipitated mass collected, dried and sublimed at 125°C to remove succinimide. The residue was recrystallized from an appropriate solvent to yield the bromo chelate.

Cu(II)(badt)Cl$_2$: This was prepared from N-chlorosuccinimide in chloroform solution by usual manner. The chlorinated chelate precipitated from chloroform-petroleum ether mixture yielded green crystals.

Cu(II)(badt)I$_2$: The reagent monopyridineiodine(I) chloride was prepared by literature methods[21, 22]. An ethanolic solution of metal chelate (20 mL, 2 mmol) was mixed with an ethanolic solution of the reagent monopyridineiodine(I) chloride (4 mmol). The solution was stirred for about 10 min, cooled in ice bath and the solution mixture poured into ice-cold water (200 mL). The solid product obtained was allowed to settle down, filtered and washed with water and dried in an oven at 80°C. The iodo compounds were recrystallized form chlorofrom-petroleum ether mixture.

TABLE-2
CHARACTERIZATION DATA FOR THE NEW HALOGENATED COMPOUNDS

Complex	Analytical data % Found (calcd.)					Colour/ state	m.p. (°C)
	C	H	N	Cu(II)	X		
$Cu(badt)Cl_2$	42.56 (42.3)	5.01 (5.29)	10.3 (10.5)	15.9 (16.0)	17.3 (17.6)	Light green powder	200–205
$Cu(badt)Br_2$	35.8 (35.5)	4.4 (4.3)	8.3 (8.6)	12.9 (13.05)	32.6 (32.8)	Green powder	170–175
$Cu(badt)I_2$	28.6 (28.9)	3.2 (3.6)	7.0 (7.2)	10.6 (10.9)	43.9 (43.7)	Light red powder	160–162

Phenylisocyanation of β-dicarbonyl chelates[23–25]: To a solution containing 2 mol of purified and vacuum dried β-dicarbonyl chelate in 50 mL dry benzene was added 4 mol of phenyl isocyanate. The reaction was topped with calcium chloride drying tube and stirred magnetically. After about 5 min a purple precipitate began to appear in a deep purple solution. After stirring at room temperature for 16 h, the solution was filtered and the precipitate was washed with 50 mL of chloroform, 50 mL of dry benzene, 50 mL of hexane in that order. The product was then dried overnight under high vacuum at 60°C.

TABLE-3
ELEMENTAL ANALYSIS FOR THE PHENYL ISOCYANATO COMPOUNDS

Compound	Analytical data %, found (calcd.)				Colour	m.p. (°C)
	C	H	N	M		
$Cu(badt)(PhNCO)_2$	59.5 (59.3)	5.3 (5.8)	12.0 (12.3)	11.5 (11.2)	Pink	165
$Ni(badt)(PhNCO)_2$	59.5 (59.8)	6.1 (5.8)	12.26 (12.46)	10.64 (10.44)	Brown	170

RESULTS AND DISCUSSION

All the parent chelates and related chelates gave elemental analyses which are in good agreement with the proposed structures (Table 1 to 3). All these chelates are coloured crystalline compounds in nature and soluble in common organic solvents. The parent chelates are highly soluble in organic solvents. The Λ_m of the parent and reacted complexes (*ca.* 2 ohm^{-1} cm^2 mol^{-1} of 10^{-4} m solution) indicate their neutral nature.

The magnetic moments of copper(II) chelates μ_{eff} are determined by the Gouy technique at room temperature varying from 1.89 to 1.91 B.M. These values are well within the range expected for magnetically dilute square-planar Cu(II) complexes. By correlating with the electronic spectra, the complexes show bands at 45450, 38750, 30300 and 15380 cm^{-1}. The band at 15380 cm^{-1} corresponds to the expected *d-d* transition of the square-planar geometry of the Cu(II) complexes[26]. Therefore the electronic and magnetic susceptibility deductions are indicative of overall square-planar metal-ligand geometry to the resultant complexes.

Diamagnetic nature of the Ni(II) chelates as evidenced by their magnetic moments suggests them to have a square-planar geometry around Ni(II). This is supported by the *d-d* electronic transition at 20400 cm^{-1} as a shoulder. This is the characteristic band of the square-planar complexes. Other transitions in the region *ca.* 28000, 32000 and 390000 cm^{-1} are possibly due to π-π* transitions. The resemblances of the electronic spectra of the reacted chelates on the parent complexes show a structural similarity[27].

Metal-ligand bonding bonding mode of the parent metal(II) chelates: The IR absorption spectra of one of the metal complexes exhibit strong bands in the region around 1535–1513, 1616–1560, 3482–3454 and 3376 cm^{-1} are assignable to coordinated ν(CO), coordinated ν(CN) and coordinated ν(NH) of bridged imine protons respectively[2–11, 14, 25] (Table-4). The parent metal(II) chelates of nickel and copper exhibit IR frequencies in the region 786–782 cm^{-1}, 1275–1026 cm^{-1} are assignable to π(CH) and δ(CH)of the reactive methine protons of the chelate rings respectively[17, 28, 29].

TABLE-4
CHARACTERESTIC IR FREQUENCIES (cm^{-1}) OF PARENT AND REACTED CHELATES

Complexes	ν(CO)	ν(CN)	π(CH)	δ(CH)	ν(NH) bridged imine proton	ν(CO) amido	ν(NH) amido
Ni(badt)	1513 s	1591 m	780 m	1026 s	3376 m, b	—	—
Ni(badt)Cl$_2$	1513 s	1609 m	—	—	3405 m, b	—	—
Ni(badt)Br$_2$	1513 s	1616 m	—	—	3398 m, b	—	—
Ni(badt)I$_2$	1513 s	1616 m	—	—	3397 m, b	—	—
Ni(badt)(PhNCO)$_2$	1513 s	1615 m	—	—	3431–3376 m, b	1750 s	3500–2921 m, b
Cu(badt)	1530 s	1577 m	782 m	1275 s	3398 m, b	—	—
Cu(badt)Cl$_2$	1530 s	1560 m	—	—	3454 m, b	—	—
Cu(badt)Br$_2$	1535 s	1560 m	—	—	3480 m, b	—	—
Cu(badt)I$_2$	1529 s	1595 m	—	—	3431 m, b	—	—
Cu(badt)(PhNCO)$_2$	1530 s	1580 m	—	—	3420 m, b	1680 s	3650–2921 m, b

All the halogenated complexes after systematic analyses proved the presence of Cl, Br, I in the ring. All the halogenated derivatives of Ni(II) and Cu(II) complexes show distinct absence of IR bands which are characteristic of π(CH) and δ(CH) of the γ(CH) protons of the chelate rings. Hence this is a direct evidence to prove that ν(CH) is substituted by γ(CX) (X═Cl, Br, I)

Comparing ^{1}H NMR signals of diamagnetic parent Ni(II) complexes and halogenated complexes, one significant feature is found. All halogenated and isocyanated complexes of Ni(II) chelate show the disappearance of *gammanu*(CH) proton (5.1 δ) indicating γ(CH) substitution. Further halogenated Ni(II) chelate exhibits ^{1}H NMR signal of bridged N—H proton, indicating the fact that polymine bridged N—H protons are not substituted by halogens.

Nature of bonding of phenyl isocyanated complexes: Phenylisocyanation reaction conducted on Ni(II)(badt), Cu(II)(badt) complexes exhibit the same spectral data. All phenylisocyanated complexes show the disappearance of IR bands characteristic of π(CH) and δ(CH). Similarly ^1H NMR spectra of Ni(II)(badt)$(PhNCO)_2$ show the disappearance of γ(CH) protons of Ni(badt) complex. Hence the above evidences indicate γ(CH) substitution. The reacted phenylisocyanato complexes show new IR frequencies in the region 1750–1680 cm^{-1} and 3650–2921 cm^{-1} respectively indicating the presence of ν(CO) amido ν(NH) amido[2, 17, 25–27].

In order to support the above statement, ^1H NMR spectrum of Ni(II)(badt)$(PhNCO)_2$ exhibit the presence of proton NMR signals ν(NH) amido (7.81 δ) and aromatic protons (7.1 δ). Hence, the above spectral data clearly indicate that the phenylisocyanate attacks at γ(CH) of the new metallic chelates and after prototropic rearrangement forms phenylamido substituted derivatives[2, 17, 25–27].

Based on the above discussion, the following tentative structures are assignable to halogenated and phenyl isocyanated complexes.

As indicated ion our earlier findings[27–29], Cu(II) chelates react much faster than Ni(II) substantiating the fact that d^9 Cu(II) system reacts faster than d^8 Ni(II) system, stating that d^n system of transition metal ion decides the reactivity of

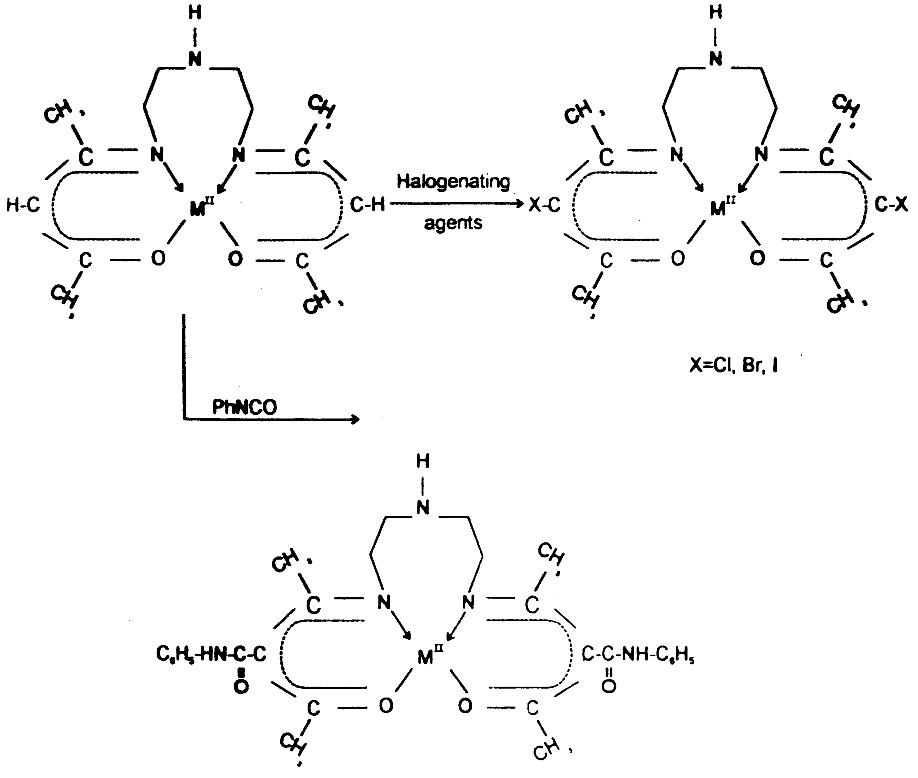

TABLE-5

SELECTED ^{1}H NMR SPECTRAL SIGNALS (δ_{ppm}) of Ni(II) COMPLEXES

S. No.	Complex	$-N{=}\underset{\vert}{C}-CH_3$	$O{=}\underset{\vert}{C}-CH_3$	γ(C—H)	Diamine proton	Bridged N–H proton	ν(N—H) amido proton	Aromatic proton
1.	Ni(badt)	2.17 (s, 3)	2.31 (s, 3)	5.1(d, 2)	3.17 (m, 8)	8.58 (b, 1)	—	—
2.	Ni(badt)Cl_2	2.20 (s, 3)	2.35 (s, 3)	—	3.18 (m, 8)	8.58 (b, 1)	—	—
3.	Ni(badt)Br_2	2.20 (s, 3)	2.36 (s, 3)	—	3.18 (m, 8)	8.58 (b, 1)	—	—
4.	Ni(badt)I_2	2.30 (s, 3)	2.34 (s, 3)	—	3.19 (m, 8)	8.58 (b, 1)	—	—
5.	Ni(badt)$(PhNCO)_2$	2.30 (s, 3)	2.35 (s, 3)	—	3.20 (m, 8)	8.58 (b, 1)	7.81 (b, 2)	7.1 (m, 10)

s = singlet, d = doublet, m = multiplet, b = broad.

coordinated ligands. Bivalent quadridentate Schiff base chelates involving different polyamine bridge are also under further investigation.

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REFERENCES

1. J.P. Collman, in: R.L. Carlin (Ed.), Transition Metal Chemistry, Marcel-Dekker, Vol. 2, p. 1 (1966).
2. V. Balasubramanian, N.S. Dixit and C.C. Patel, *J. Inorg. Nucl. Chem.*, **41**, 122 (1979).
3. R.W. Kluiber, *J. Am. Chem. Soc.*, **82**, 4839 (1960).
4. J.P. Collman and E.T. Kittleman, *Inorg. Chem.*, **1**, 499 (1962).
5. Y. Fujii, *Bull. Chem. Soc. (Japan)*, **43**, 1722 (1970).
6. A. Kasahara and T. Izvmi, *Bull. Chem. Soc. (Japan)*, **41**, 2185 (1968).
7. C.J. Hipp and D.H. Bush, *Inorg. Chem.*, **11**, 737 (1972).
8. ———, *Inorg. Chem.*, **12**, 894 (1973).
9. K.P. Balakrishnan and V. Krishnan, *Curr. Sci. (India)*, **46**, 655 (1977).
10. A. Singh and B. Hirsch, *Indian J. Chem.*, **8**, 756 (1970).
11. K.P. Balakrishnan and V. Krishnan, *Synth. React. Inorg. Met-Org. Chem.*, **8**, 227 (1978).
12. R.H. Holm and G.W. Everett (Jr.) and A. Chakravarthy, *Prog. Inorg. Chem.*, **7**, 82 (1966).
13. J.P. Collman, *Adv. Chem. Sci.*, **37**, 37 (1963).
14. K.P. Balakrishnan and V. Krishnan, *Synth. React. Inorg. Met-Org. Chem.*, **9**, 109 (1979).
15. J.P. Dix and F. Vogtle, *Angew. Chem. Int. Ed. Engl.*, **17**, 857 (1978); *Chem. Ber.*, **113**, 457 (1980).
16. P.J. McCarthy, R.J. Hovey, K. Veno and A.E. Martel, *J. Am. Chem. Soc.*, **77**, 5820 (1955).
17. V. Balasubramanian, A. Loganayagi, R. Nanthini, A. Ravi, N. Karthikeyan and S. Muthu Kumaran., *Asian J. Chem.*, **15**, 126 (2003).
18. J.P. Collman and R.A. Moss, *J. Am. Chem. Soc.*, **83**, 531 (1961).
19. L.F. Lindoy, Hyacinth and C. Lip, *J. Chem. Soc. Dalton*, **44** (1974).
20. S.K. Ramalingam and K. Jeyasubramanian, *Indian J. Chem.*, **31A**, 702 (1992).
21. P.R. Singh and R. Sahai, *Aust. J. Chem.*, **20**, 639 (1967).
22. P.N. Howells and J.W. Kenny, *Inorg. Chem.*, **15**, 124 (1967).
23. S.A. Samath and N. Raman, *Polyhedron*, **11**, 33 (1992).
24. V. Balasubramanian and C.C. Patel, *Synth. React. Inorg. Met-Org. Chem.*, **12**, 11 (1982).
25. V. Balasubramanian, R.R. Iyengar and C.C. *Patel, Proc. Indian Acad. Sci. (Chem. Sci.)*, **90**, 33 (1981).
26. V. Balasubramanian, "The reactions of coordinated ligands", Ph.D. Thesis, Indian Institute of Science, Bangalore (1980).
27. N.S. Dixit, B.P. Sudha and C.C. Patel, *Bull. Chem. Soc. (Japan)*, **51**, 2160 (1978).
28. V. Balasubramanian, N.S. Dixit and C.C. Patel, *Indian J. Chem.*, **20A**, 667 (1981).
29. V. Balasubramanian, A. Loganayagi, M. Muneeswaran and N. Karthikeyan, *Asian J. Chem.*, **12**, 157 (2000).

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