REACTIONS OF TRICYCLIC TETRADENTATE β-KETOIMINE COMPLEXES OF NICKEL(II) AND COPPER(II) IONS WITH ARYLDIAZONIUM CHLORIDES

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ELECTROPHILIC substitution reactions of coordinated β-diketones are well known[1-2]. Their reactivity stems mainly from the 'quasiaromaticity' of the chelate ring. Similar studies have also been extended to a few monovalent β-ketoimine complexes[3-8]. However, no comprehensive investigation of reactions of bivalent quadridentate Schiff base-metal complexes derived from β-diketones and 1,2-diamines has been done.

Herein, we report a novel type of reaction of bivalent tricyclic tetradentate β-ketoimine complexes of Ni(II) and Cu(II) with phenyldiazonium chloride. The diazonium coupling reaction occurs on the γ-carbon atom of the chelated ring.

EXPERIMENTAL

N,N'-ethylene-bis(acetylacetoneimino)metal(II) complexes, M (AE) were prepared by the usual method[9].

A solution of M (AE) (0·01 mole) and sodium acetate (0·1–0·2 mole, to keep the pH around 2·6–3·0) in methanol was cooled to 0° C. This was treated with aqueous phenyldiazonium chloride (0·02 mole) dropwise with continuous stirring. The crystals of the complexes obtained were collected by filtration, washed with water and recrystallised from chloroform-methanol mixture. The reaction of M (AE) with phenyldiazonium chloride in equimolar ratio afforded mono-diazo coupled complexes. The general pattern of the reaction is shown below.
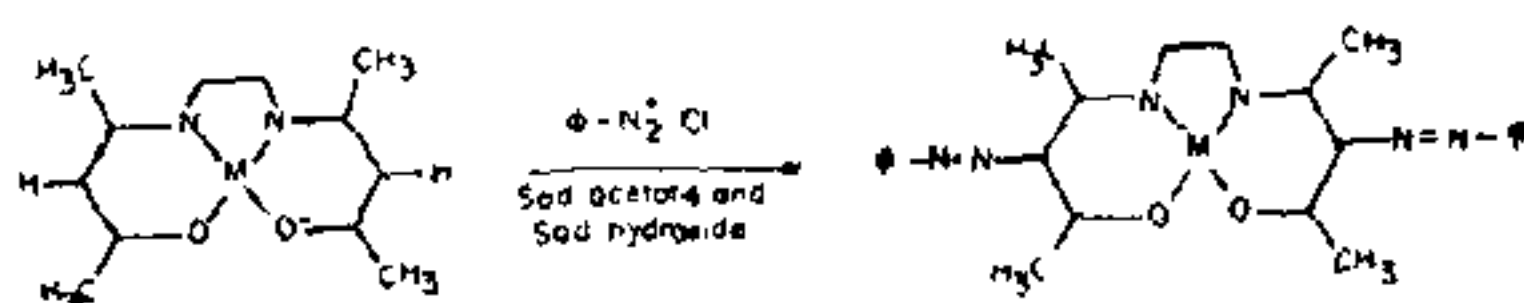
Typical analytical data of some of the complexes is given in Table I.

RESULTS AND DISCUSSION

The complexes gave satisfactory elemental analysis corresponding to the mono- and di-diazo coupled complexes. They are deeply coloured, crystalline, stable and have good solubility in both polar and non-polar solvents. Ni(II) complexes are diamagnetic implying planar geometry around the metal-ion. Cu(II) complexes are paramagnetic (ca. μ_{eff} 1·73 B.M.) which indicates square planar environment around Cu(II) ion.

The substitution of γ-CH carbon proton by the phenyl-diazonium group was confirmed by the absence of ir absorptions around 762 cm^{-1} (s) and 1190 cm^{-1} (vw) due to the out-of-plane and in-plane vibrations of the ring-CH respectively and also the absence

Analytical data

Compound	C (%)	H (%)	N (%)	M (%)
Ni (AE) (N₂ph)₂	58·33	5·20	16·90	11·83
C₂₄H₂₂N₆O₂Ni	(58·9)	(5·35)	(17·18)	(11·90)
Ni (AE) (N₂ph-*p*-CH₃)₂	59·32	5·60	15·99	11·23
C₂₂H₃₃N₆O₂Ni	(60·30)	(5·80)	(16·20)	(11·34)
Ni (AE) N₂ph	56·21	5·63	14·39	15·19
C₁₈H₂₂N₄O₂Ni	(56·13)	(5·75)	(14·55)	(15·24)
Cu (AE) (N₂ph)₂	58·24	5·32	16·90	12·80
C₂₄H₂₆N₆O₂	(58·34)	(5·30)	(17·01)	(12·85)
Cu (AE) (N₂ph-*p*-CH₃)₂	59·20	5·31	16·36	12·29
	(59·80)	(5·02)	(16·10)	(12·16)

Theoretical values are given in parentheses.

of the ring -CH proton signal in the PMR spectra of the Ni(II) complexes. The ir spectra of both Cu(II) and Ni(II) complexes show v (C=N) and v (C—O) around 1645 cm^{-1} (s) and 1540 cm^{-1} (s) respectively. Slight increase in both of these frequencies are ascribed to the attachment of electronegative phenyldiazo group to the chelate ring.

The diazo-substituted β-ketoimine complexes of Ni(II) show no signal at 4·93 δ in the PMR spectra. This suggests that the substitution had occurred at the γ-carbon atom of the chelated ring. The signal due to the protons of the phenyl group occurs as a complex multiplet centered at 7·03 δ. The methyl protons resonate at 2·4 δ (—N=C)–CH₃ and 2·5 δ (–O–C)–CH₃. The signal due to the diamine skeleton protons gives a complex multiplet (possibly AA' BB' spin system) at 3·4 δ.

We now adduce evidence that the diazonium coupling reaction proceeds selectively. This is demonstrated by the synthesis of mono diazosubstituted β-ketoimine complexes. The ir spectra of these complexes show bands around 762 cm^{-1} (s) and 1190 cm^{-1} (vw) due to the out-of-plane and in-plane vibration of γ-(CH), respectively. Four bands are observed in the 1500–1700 cm^{-1} region of the ir spectra of these complexes. The bands at 1638 cm^{-1} (s), 1591 cm^{-1} (s) and 1566

cm^{-1} (s), 1520 cm^{-1} (s) are respectively, due to ν (C=N) and ν (C-O) of the diazo-substituted and non-substituted chelated ring of the complexes. The Proton Magnetic Resonance Spectra of the Ni(II) complexes also show signals due to one γ-CH proton (4·9δ singlet) and five protons of the phenyl group (7·33δ multiplet), thereby confirming the nature of the substituted products. The generality of these reactions has been tested for both Ni(II) and Cu(II) complexes of the β-keto-imines.

It is worthwhile to point out that the diazonium coupling reaction presented here is not only novel but opens up a new area towards the synthesis of metal-ion containing dyes.

Acknowledgements

1. Collman, J. P., *Adv. Chem. Ser.*, 1968, 37, 78.
2. —, *Transition Metal Chemistry*, Marcel Dekker, New York, 1966, 2, 1.
3. Kluiber, R. W., *J. Am. Chem. Soc.*, 1960, 92, 8889.
4. Collman, J. P. and Kittleman, E. T., *Inorg. Chem.*, 1962, 1, 499.
5. Fujii, Y., *Bull. Chem. Soc., Japan*, 1970, 43, 1722.
6. Kasahara, A. and Izumin, T., *Ibid.*, 1968, 41, 2185.
7. Hipp, C. J. and Busch, D. H., *Inorg. Chem.*, 1972, 11, 737.
8. — and —, *Ibid.*, 1973, 12, 894.
9. McCarthy, P. J., Hovey, R. J., Ueno, K. and Martell, A. E., *J. Am. Chem. Soc.*, 1955, 77, 5820.

ON THE MEASUREMENT OF RELATIVE OSCILLATOR STRENGTHS

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Abstract

A method is indicated for determining the relative oscillator strengths for different lines using atomic absorption spectrophotometry. The method is applicable to a wide range of resonance lines which show similar hyperfine structure effects, and is free from systematic errors associated with the calibration of apparatus. The relative 'f' values for the lines Ag-3383, Cu-3274, Mn-4030, Mn-3217, Sb-2127, Eu-3334, Tm-5307 and Yb-2673 have been estimated.

1. Introduction

COMMON methods for the measurement of oscillator strengths (f-values) include anomalous dispersion[1], absorption in optically thin layers[2] and emission measurements[3]. Ostroymenko and Rossikhin[4] used the method of line absorption for estimating Nf taking into account differences in the emission/absorption width ratios (α-values). However, as stated by L'vov[5], this is unnecessary in the calculation of relative f-values. He proposed the measurement of these quantities from the analytical sensitivities obtained in flames. A slightly different approach for obtaining relative f-values for resonance absorption lines of an element showing similar hyperfine structure is indicated in this note.

2. Principle

Consider the absorption of a beam of resonance radiation of frequency ν, through a cell containing a metal vapour at temperature T (and having vapour press p in atmospheres), such that similar situations exist in the emitting and absorbing gas and only heat motions of the atoms are taken into account. The peak absorption coefficient is defined as[6]:

$$K_\nu^0 = \sqrt{\frac{\pi M}{2RT}} \cdot \frac{e^2}{m\nu_0} \cdot Nf \tag{1}$$

where the symbols have their usual meaning. On introducing the appropriate values of various constants and using ideal gas laws, one obtains

$$K_\nu^0 = \frac{8 \cdot 512 \times 10^{15} pf \sqrt{M}}{\nu_0 T^{3/2}} \tag{2}$$

writing the absorbance in $I/I_0 = A_T$

$$A_T = K_\nu^0 \cdot le^{-w^2} = K_\nu^0 \cdot L \tag{3}$$

If a constant K_p is introduced such that,

$$K_p = \frac{\nu_0}{8 \cdot 512 \times 10^{15} f \sqrt{M} L} \tag{4}$$

Combination of (2), (3) and (4) gives,

$$p = K_p A_T T^{3/2} \tag{5}$$