

Synthesis and study of cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 2-formyl- and 2-acetyl-cyclohexanones

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Metal(II) complexes of the type $ML_2nB[M = \text{Co(II), Ni(II), Cu(II) and Zn(II)}; L = \text{2-formyl- or 2-acetyl-cyclohexanone}; B = \text{H}_2\text{O, Py}; n = 0, 2]$ have been prepared and characterized by elemental analyses, molar conductance, IR, electronic and NMR spectra, and magnetic susceptibility studies. The copper complexes possess square-planar geometry whereas the nickel and cobalt diaquates possess octahedral environment. The corresponding anhydrides are polymeric and possess high-spin octahedral configuration. All the base adducts possess high-spin octahedral configuration with a tendency towards dissociation in solution. IR and PMR spectra of the ligands and complexes indicate that the formylcyclohexanone coordinates in the hydroxymethylene form whereas the acetylcyclohexanone coordinates in the cyclohexene form. The order of the stabilities, namely $\text{Cu} > \text{Ni} > \text{Co} > \text{Zn}$, derived from $\nu(\text{M}-\text{O})$, parallels the crystal field stabilization energy.

Cobalt(II), nickel(II) and copper(II) chelates of most β -diketones¹ and *o*-hydroxyarylcarbonyl compounds² are obtained usually as dihydrates in which the metal ions have high-spin octahedral configuration. All the anhydrous copper(II) species possess a square-planar structure, whereas the respective nickel(II) and cobalt(II) complexes are polymeric, high-spin octahedral species. It may be noted that even when a benzene or naphthalene ring (resonating π -system) is fused to the hetero chelate ring, a lowering of stability is noted. This implies that $\text{C}=\text{O}$ group is not well conjugated with the aryl group³. The effect of the conjugation of $\text{C}=\text{O}$ with the external $\text{C}=\text{C}$ on the structure of the complexes have been investigated by our group⁴⁻⁶. We thought it of interest to study the effect of fusion of alicyclic ring with the chelate ring on the structure and stability of the metal chelates. 2-Formylcyclohexanone and 2-acetylcyclohexanone have been chosen for this purpose, as the former has received scant attention as a ligand⁷ and the latter has been used in the determination of formation constants of complexes only⁸. In this paper we report the synthesis and characterization of metal chelates of 2-formyl- and 2-acetylcyclohexanones, their adducts and the correlation between their stabilities and $\nu(\text{M}-\text{O})$ values.

Materials and Methods

Metals were determined by EDTA titration after decomposing the complexes with conc. HNO_3 and H_2O_2 , or gravimetrically as oxides by incinerating the metal complexes with an excess of $(\text{NH}_4\text{O}_2\text{C})_2\cdot\text{H}_2\text{O}$. C, H and N analyses were carried out at the VHNSN

College, Virudhunagar, India. Magnetic susceptibilities were measured at 302-304 K and at 8000 G in a Gouy balance calibrated against $\text{Hg}[\text{Co}(\text{CNS})_4]$. IR spectra ($4000\text{-}200\text{ cm}^{-1}$) were recorded in the KBr phase on a Perkin-Elmer 577 grating spectrophotometer. Electronic spectra were measured in CHCl_3 , ethanol and pyridine using a Perkin-Elmer 402 UV-VIS spectrophotometer and Bousch and Lomb spectronic 2000 spectrophotometer. Conductance measurements were made on $1 \times 10^{-3}\text{ M}$ methanol solutions of the complexes on a Toshniwal conductivity meter. Molecular weights of the complexes were determined cryoscopically in diphenyl (71°). PMR spectra were obtained in CDCl_3 or $\text{DMSO}-d_6$, with TMS as the internal standard on a Perkin-Elmer R32, 90 MHz spectrometer. All the chemicals used were of AR grade except sodamide (Aldrich Co.), pyridine and ethyl formate which were of reagent grade.

Syntheses of ligands

2-Formylcyclohexanone (FCH) was prepared adopting the method reported in the literature⁹ from a mixture of cyclohexanone, ethyl formate and metallic sodium in dry ether (b.p. $74\text{-}75^\circ$; 5.5 mm). 2-Acetylcyclohexanone (ACH) was obtained from a mixture of cyclohexanone, ethyl acetate and sodamide in dry ether according to literature method¹⁰ (b.p. $110\text{-}11^\circ$; 20 mm).

Syntheses of complexes: $\text{CoL}_2(\text{H}_2\text{O})_2$, $\text{NiL}_2(\text{H}_2\text{O})_2$, CuL_2 , ZnL_2 , where $L = \text{FCH/ACH}$

An aqueous solution (100 ml) of metal(II) acetate (10 mmol) was added with stirring to the ligand (20

Table 1—Colour, analytical data and magnetic moments of metal(II) complexes of 2-formyl- and 2-acetyl-cyclohexanones

Ligand (L)	Formula (Colour)	% Found (Calc.)				μ_{eff} (B.M.)
		M	C	H	N	
FCH	CuL ₂ (Dark green)	20.16 (20.26)	54.15 (53.58)	6.12 (5.74)	—	1.77
FCH	NiL ₂ (Green)	18.84 (19.02)	54.82 (54.42)	5.94 (5.83)	—	2.94
FCH	CoL ₂ (Pale red)	18.67 (19.07)	55.26 (54.38)	5.13 (5.83)	—	4.91
FCH	ZnL ₂ (White)	20.90 (20.73)	54.23 (53.27)	6.31 (5.71)	—	dia
ACH	CuL ₂ (Dark green)	18.35 (18.71)	55.91 (56.55)	6.23 (5.89)	—	2.10
ACH	NiL ₂ (Pale green)	17.29 (17.54)	58.13 (57.36)	6.23 (5.97)	—	3.41
ACH	ZnL ₂ (White)	17.05 (17.15)	57.15 (56.24)	6.20 (5.86)	—	dia
FCH	NiL ₂ .2H ₂ O (Pale green)	16.98 (17.03)	48.60 (48.74)	6.45 (6.38)	—	3.23
FCH	CoL ₂ .2H ₂ O (Orange)	17.08 (17.08)	48.13 (48.70)	6.45 (6.38)	—	4.61
ACH	NiL ₂ .2H ₂ O (Pale green)	14.98 (15.79)	51.35 (51.79)	6.52 (6.47)	—	3.01
FCH	NiL ₂ .Py ₂ (Grey)	12.39 (12.58)	60.52 (61.71)	5.83 (6.00)	6.12 (6.00)	2.96
FCH	CoL ₂ .Py ₂ (Orange red)	12.30 (12.62)	60.73 (61.68)	5.92 (6.00)	6.31 (6.00)	4.69
ACH	NiL ₂ .Py ₂ (Green)	11.80 (11.87)	62.67 (63.06)	6.92 (6.46)	5.12 (5.65)	3.38
ACH	CoL ₂ .Py ₂ (Orange)	11.69 (11.91)	62.50 (63.04)	5.45 (6.47)	5.93 (5.66)	4.49

mmol) in ethanol (25 ml) and the pH raised to 6-7 with aqueous NaOH. The precipitated complexes were filtered, washed successively with water, aqueous ethanol and dried *in vacuo* over CaCl₂ (yield 50-95%). A stable cobalt(II) complex could not be isolated with 2-acetylcyclohexanone.

Anhydrous NiL₂, CoL₂ complexes

These complexes were obtained by heating the diaquo complexes isothermally at 120° in air for an hour.

Pyridine adducts: NiL₂(Py)₂ and CoL₂(Py)₂

The dihydrates of nickel and cobalt complexes were dissolved in pyridine and the solutions allowed to evaporate slowly to near dryness. The resulting solids were filtered, washed with petroleum ether (b.p. 60-80°) and dried *in vacuo*.

Bis(2-acetylcyclohexanonato)dipyridinecobalt(II)

2-Acetylcyclohexanone (10 mmol) in EtOH (10 ml) and cobalt(II) chloride (5 mmol) in EtOH (10 ml)

were mixed thoroughly. To the resultant orange solution was added excess pyridine from which the adduct crystallised out on slow evaporation.

Results and Discussion

The colour of the complexes, analytical data and magnetic moment values are given in Table 1. The analytical data are consistent with the assigned formula ML₂nB.

Weight loss experiments indicated loss of water in dihydrates around 120°. The pyridine adducts lost the coordinated pyridine around 80°. The low molar conductance values ($\Lambda_M \sim 10\text{-}20 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in methanol) indicated the chelates to be non-ionic. Molecular weight measurements indicated the monomeric nature of the copper complexes and the diaquo complexes of nickel and cobalt. The observed nuclearity of 2.1-2.5 in the anhydrous complexes shows that most of the complexes may be trimeric, since the smallest possible octahedral polymer is a trimer. This parallels

the observations made on other *o*-hydroxyarylcarbonyl complexes¹¹ and acetylacetonates¹².

Magnetic properties

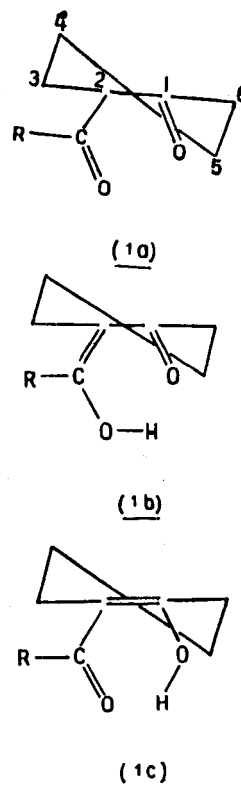
The room temperature magnetic moments of the copper complexes were found to be in the range 1.77-2.10 BM (Table 1), typical of square-planarity. The magnetic moments of the anhydrous nickel complexes, diaquates and dipyridinates were found to be in the range 2.94-3.41 BM which are indicative of their six-coordinate octahedral geometry¹². All the cobalt complexes showed magnetic moments in the range 4.49-4.91 BM which are somewhat low for truly octahedral complexes but are suggestive of distorted structure. The loss of degeneracy of $^4T_{1g}$ ground term as result of symmetry lower than octahedral, followed by partial quenching of the orbital contribution, is expected to yield magnetic moments lower than those for truly octahedral species¹³.

Ligand field spectra

The electronic absorption spectra of the copper complexes showed bands in the regions 14235-15200 and 18180-18215 cm^{-1} which are assigned to $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2E_{1g}$ transitions, respectively, characteristic of square-planar environment¹⁴. All the anhydrous compounds, dihydrates and dipyridinates of nickel(II) and cobalt(II) exhibited ligand field bands consistent with octahedral stereochemistry. The nickel(II) complexes manifested two bands around 14860-15870 and 22270-27030 cm^{-1} assignable respectively to $^3A_{2g} \rightarrow ^3T_{1g}$ and $^3A_{2g} \rightarrow ^3T_{1g} (P)$ transitions. The cobalt complexes showed bands in the regions 17095-18820 and 19050-23585 cm^{-1} which can be ascribed to $^4T_{1g} \rightarrow ^4A_{2g}$ and $^4T_{1g} \rightarrow ^4T_{1g} (P)$ transitions respectively. The low energy band could not be recorded in our spectrophotometer. In pyridine, the ν_2 and ν_3 bands of cobalt and nickel complexes shifted to higher frequencies with a change in ϵ , indicating adduct formation. The spectra of the base adducts of nickel and cobalt in CHCl_3 or ethanol resembled those of anhydrous species and this may be due to their dissociation to anhydrous species in solution.

Infrared and NMR spectra

Three tautomeric forms are possible for the ligands under study (structures 1a, b, c). A high resolution NMR study revealed that 2-formylcyclohexanone exists in the keto form (1b), viz., 2-hydroxymethylenecyclohexanone¹⁵ while 2-acetylcyclohexanone exists in the enol form (1c), viz., 2-acetylcyclohexene-1-ol¹⁶. Because of the most likely half-chair conformation¹⁷ for this molecule, carbon atoms 1, 2, 3 and 6 lie in the



same plane which makes the coordination feasible, which otherwise would be impossible.

The OH stretch occurred as a broad shallow band around 3000 cm^{-1} characteristic of β -diketone (enol) chelates. The presence of enolic form was supported by the appearance of a broad ^1H NMR signal at δ 14.5 ppm for 2-formylcyclohexanone and at δ 15.7 ppm for 2-acetylcyclohexanone. The NMR spectrum of $\text{Zn}(\text{FCH})_2$ showed peaks at the following positions: δ 8.35 ppm (s, vinylic proton), δ 2.35, 1.75 ppm (m, ring protons). The absence of absorption at δ 14.5 ppm indicated that the coordination occurred through the loss of enolic proton. The other signals in the complex occurred almost in the same positions as in the ligand. This leads to the conclusion that the hydroxymethylene form (1b) is retained in the complexes also.

The broad intense absorption in the region 1640-1540 cm^{-1} in formylcyclohexanone and in the region 1660-1500 cm^{-1} in acetylcyclohexanone may be ascribed to the presence of chelated $\nu(\text{C}=\text{O})$. $\nu(\text{C}-\text{O})$ occurred at 1310 cm^{-1} in FCH and at 1355 cm^{-1} in ACH. In contrast to the simple β -diketonates, the two ligand oxygen atoms of alicyclic β -diketonates are not equivalent. This may be due to the effect of bond fixation in the chelate ring produced by the fusion of alicyclic ring as in the case of *o*-hydroxyarylcarbonyl complexes³. In all the metal complexes,

$\nu(\text{C}=\text{O})$ got shifted to lower frequency and $\nu(\text{C}-\text{O})$ to higher frequency, indicating the carbonyl and enolic oxygen coordination to the metal. It is noteworthy that $\nu(\text{C}=\text{C})$ could not be observed in the FCH complexes because of its possible merger with the intense $\text{C}=\text{O}$ band, whereas it was observed as a separate band in the $1622\text{--}1615\text{ cm}^{-1}$ region in ACH complexes. The difference in the IR spectra with respect to $\nu(\text{C}=\text{C})$ may be due to the difference in the tautomeric forms involved in coordination and it may be tentatively said that in ACH complexes the ligand coordinates in the cyclohexene form with an endocyclic double bond (1c). Due to poor solubility the NMR spectrum of $\text{Zn}(\text{ACH})_2$ could not be recorded.

The νOH of water appeared around 3000 cm^{-1} in the dihydrates of nickel and cobalt. The bands around 500 cm^{-1} were found to be metal-sensitive and they are tentatively assigned to $\nu(\text{M}-\text{O})$. The values of $\nu\text{M}-\text{O}$ follow the crystal field stabilization energy order^{18,19}, viz., $\text{Cu} > \text{Ni} > \text{Co} > \text{Zn}$. The $\nu(\text{M}-\text{O})$ values for acetylacetonone complexes are greater ($33\text{--}60\text{ cm}^{-1}$) than those of formylcyclohexanone complexes and this reveals the greater stability of the frequencies.

Effect of adduct formation

Compared to the dihydrates, the anhydrides showed $\nu(\text{C}=\text{O})$ and $\nu(\text{M}-\text{O})$ at lower frequencies. The lower $\nu(\text{C}=\text{O})$ should lead to a higher $\nu(\text{M}-\text{O})$. The observed lower $\nu(\text{M}-\text{O})$ is ascribed to the bonding of carbonyl oxygen to two metal ions in a polymeric structure¹², in contrast to the bonding in the monomeric structure of the dihydrates where one metal ion is coordinated to the carbonyl oxygen.

The copper complexes did not show any tendency towards adduct formation because of Jahn-Teller stabilization. The replacement of water by pyridine in cobalt and nickel complexes caused $\nu(\text{C}=\text{O})$ to decrease ($12\text{--}20\text{ cm}^{-1}$), $\nu(\text{C}-\text{O})$ to increase ($2\text{--}65\text{ cm}^{-1}$) and $\nu(\text{M}-\text{O})$ to decrease ($7\text{--}12\text{ cm}^{-1}$). The pyridine

addition depletes the electron density of both the $\text{M}-\text{O}$ and $\text{C}=\text{O}$ bonds and this is consistent with the π -acceptor properties of pyridine. Similar effects have been observed for the pyridine adducts of uranyl β -ketoenolates¹⁸.

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