

Complexes of Nickel(II) with *o,o'*-Dihydroxy Chalkones

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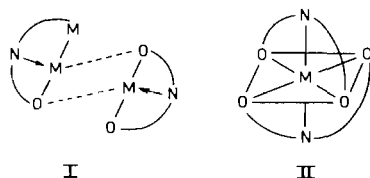
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A few nickel(II) complexes have been prepared by reacting sodium salts of *o,o'*-dihydroxy chalkones with nickel compounds in aqueous alcohol medium. The complexes are characterised by elemental analysis and are shown to possess 1:1 stoichiometry. Magnetic data, electronic and infrared spectra show that nickel, in these complexes exhibits coordination number four and appears to have tetrahedral configuration.

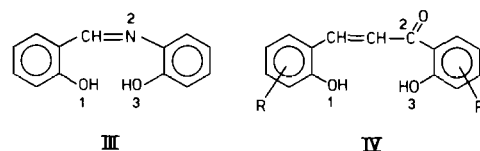
Introduction

The traditional tridentate ligands having two active centres and one coordinating centre, containing either ONO, or ONS or SNS sequences and their complexes with transition metals rank amongst the most studied and well characterised ones¹. These bases show a special preference to the formation of dimeric complexes (I) and dimeric copper, nickel and oxovanadium(IV) are well documented in the literature². Quite a good number of hexa coordinated complexes are cited in the literature³, having structure (II). Recently,



Biradar and coworkers⁴ have isolated monomeric hexacoordinated complexes of titanium(IV) with the bases containing ONO sequences⁵. The dual behaviour encountered in such ligands has made us to search for a new system which is almost similar in geometry to this kind of ligands.

The ligands synthesized contain –O,O,O– sequences as against the usual –ONO– sequences of the typical tridentate ligands. The chalkones (IV) resulted by the condensation of *o*-hydroxy-substituted acetophenones with *o*-hydroxy-substituted benzaldehydes constitute this class of tridentate ligands.

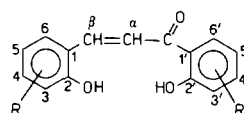


In these ligands, two are active centres (1 and 3) and (2) is a coordinating centre. The active centre (3) and coordinating centre (2) are connected together with the active centre (1) via unsaturated ethylenic bridge (–C=C), which imposes strain on the ligand while forming the complexes. As a result of this strain the OH(3) and C=O(2) groups may attach themselves to the same metal ion while the OH(1) may not attach itself to the same metal ion, or both OH and C=O may attach to the same metal ion and annule the strain.

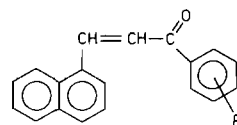
It is, therefore, assumed that, to maintain the covalency and to attain the stable geometry, the complexes formed may undergo dimerisation. To verify the accuracy of our assumption, we have undertaken a systematic study of transition metal complexes with the chalkones (V–XII) shown below.

There appears to be a few reports about the chalkone complexes in the literature^{6,7}. This has prompted us to have further probe into the elucidation of the structure and geometry of the complexes.

In this paper we wish to report the synthesis and spectral studies of a few nickel(II) complexes with chalkones (V–XII).



	R	R'
V	H	5'-Me
VI	5-Me	5'-Me
VII	5-Cl	5'-Me
VIII	H	5'-Cl
IX	5-Me	5'-Cl
X	5-Cl	5'-Cl



XI	5'-Me
XII	5'-Cl

Experimental

Materials and Method

2-Hydroxy-5-methyl-acetophenone and 2-hydroxy-5-chloro-acetophenone were prepared starting with *p*-cresol and *p*-chloro-phenol, subjecting them to acetylation followed by Fries migration.

5-Methyl- and 5-chloro-salicylaldehydes and 2-hydroxynaphthaldehyde were prepared by Duff's method⁸.

The chalcones V–XII were prepared by the method reported by Dhar⁹ and recrystallised from benzene.

Nickel chloride used for preparing the complexes was an Analar BDH reagent.

General Method of Preparation

To an alcoholic solution of 0.02 mol of chalcone, was added an aqueous solution of 0.04 mol sodium hydroxide with shaking. Any sodium salt precipitated during the reaction was dissolved by adding small quantity of water. To this red solution of disodium chalconate, was added, with vigorous shaking 0.02 mol of nickel chloride in minimum quantity of water. The complex precipitated was filtered washed thoroughly with water then with alcohol and dried between 105 and 110°C.

The powdered complex was then subjected to soxhlet extraction using cyclohexane. The complex was then dried at 105–110°C.

Analysis

Nickel in the complexes was determined gravimetrically as dimethyl glyoximate. Carbon and hydro-

gen were determined by microanalytical method. The results of the elemental analyses are given in Table I.

Physical Measurements

The molar conductivities of the complexes in DMF were taken with an ELICO conductivity bridge C.M.82 having a cell of cell constant 0.829 cm⁻¹, manufactured by Electronic Industrial Instrument Co., Hyderabad.

The electronic spectra were recorded on a Beckman DB-2 using 1 cm glass cells. The infrared spectra of the ligands and the complexes in Nujol mulls were recorded respectively on Perkin–Elmer 137-B infracord and Beckman IR-18 spectrophotometers.

The magnetic susceptibilities of the complexes were determined on a Gouy balance at room temperature with a glass tube calibrated for diamagnetism.

Results and Discussion

Synthesis

Instead of repeating the method of Tsumaki *et al.*⁶, we have extended the method of preparing aldehydato complexes¹⁰ to the synthesis of nickel(II) chalconato complexes. An aqueous alcoholic solution of disodium chalconate on shaking with an aqueous solution of nickel chloride yields dark red to brownish red coloured complexes.

The elemental analysis obtained for these complexes agree well with the formulation of 1:1 type complexes (Table I). The insolubility of these complexes in most of the common organic solvents except few, *viz.*, DMF, pyridine, DMSO, makes our efforts to determine the molecular weights futile.

TABLE I. Elemental Analysis of Ni(II) Complexes with 2,2'-Dihydroxy Chalcones.^a

Lig. No.	Complexes	% Ni	% C	% H	μ_{eff} in B.M.
V	(C ₁₆ H ₁₂ O ₃)Ni · H ₂ O	17.75 (17.84)	58.17 (58.38)	4.23 (4.26)	3.97
VI	(C ₁₇ H ₁₄ O ₃)Ni · H ₂ O	16.95 (17.12)	— (59.53)	— (4.67)	3.84
VII	(C ₁₆ H ₁₁ ClO ₃)Ni · H ₂ O	16.00 (16.15)	— (52.86)	— (3.58)	3.76
VIII	(C ₁₅ H ₉ ClO ₃)Ni · H ₂ O	16.81 (16.80)	52.01 (51.54)	5.08 (4.99)	3.46
IX	(C ₁₆ H ₁₁ ClO ₃)Ni · H ₂ O	16.24 (16.15)	52.90 (52.86)	3.61 (3.58)	3.27
X	(C ₁₅ H ₈ Cl ₂ O ₃)Ni · H ₂ O	15.31 (15.29)	— (46.91)	— (2.61)	3.52
XI	(C ₂₀ H ₁₄ O ₃)Ni · H ₂ O	15.38 (15.49)	— (63.37)	— (4.23)	3.45
XII	(C ₁₉ H ₁₁ ClO ₃)Ni · H ₂ O	14.60 (14.70)	56.30 (57.11)	3.31 (3.26)	3.16

^a Values in parentheses are calculated values.

The molar conductance values obtained for $\sim 10^{-3} M$ solutions are too small to account for any dissociation of the complexes in DMF. Hence these may be looked upon as non-electrolytes.

Magnetic Data

The magnetic moments obtained at room temperature for these nickel(II) complexes are listed in Table I. The μ_{eff} values fall in the range of 3.16 to 3.97 BM. The theory predicts that, because of the high orbital contribution to the magnetic moments, the nickel(II) in tetrahedral environment shows moments in the range of 3.5 to 4.2 BM¹¹. It may, therefore, be concluded that nickel(II) has tetrahedral environment in these complexes.

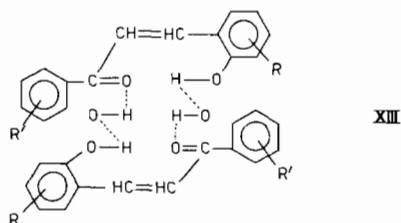
Electronic Spectra

The electronic spectra of nickel(II) complexes under present investigation display two bands in the 610–630 nm. region. It is documented in the literature that tetrahedral nickel(II) complexes show high intensity bands in the regions 600–700 and 1250–1400 nm¹¹. The observed high intensity of the band in the region 610 to 630 nm and the absence of the band around 400 nm have made us to conclude that nickel(II) may have in these complexes a tetrahedral configuration. The high intensity band in the above region is ascribed to ${}^3T_1(F) \rightarrow {}^3T_1(P)$ transition. The splitting observed in this band may be due to the spin orbit coupling.

Infrared Spectra

The infrared frequencies of the ligands and their nickel(II) complexes are systematised, respectively, in Tables II and III.

It is well established that the hydrogen bonding reflects on the weakening and broadening of the band and shifts it to the lower frequency¹², depending on the strength of the bond. In all the spectra of the ligands, we observe a broad weak band around 2650 cm^{-1} and is attributed to the intramolecular hydrogen bonded –OH. This band is absent in benzalacetophenone and benzylideneaniline. In addition to this band we notice a medium intensity broad band in the region 3300–3200 cm^{-1} and is ascribed to the intermolecular hydrogen bonded –OH on analogy with the intermolecular hydrogen bonded –OH of aldoximes¹³. The absence of this band in 2-methoxy-2'-hydroxy-5'-methyl and 2-methoxy-2'-hydroxy-5'-chloro-chalkones confirms the assignment.



In the complexes the band around 2650 cm^{-1} disappears, and in the place of 3300–3200 cm^{-1} medium intensity band, we observe a sharp–broad band in the region 3400–3350 cm^{-1} . The free hydroxy group and water of hydration give rise to a sharp narrow band in the region 3590–3490 cm^{-1} . The drying of weighed sample for 2 to 3 hr at 120°C does not cause any decrease in the weight of the complex taken for the purpose. This indicates that the complexes do not contain any loosely bound water molecule. The appearance of the broad band in the lower frequency region conveys that the complexes may contain water molecule coordinated to the metal ion. The removal of water at elevated temperature and consequent decomposition of the complexes confirm the above conclusion.

The region prescribed for the $\nu(\text{C}=\text{O})$ stretching is 1700–1650 cm^{-1} ¹⁴. Thomson and Torkington¹⁵ have shown that conjugation of C=O group with C=C results in shifting of the $\nu(\text{C}=\text{O})$ to the lower frequency. Dhar and Gupta¹⁶ have observed this band at 1665 cm^{-1} in chalkones. In these 2,2'-dihydroxy chalkones (V–XII), we observe an intense band in the region 1650–1639 cm^{-1} due to C=O stretch. The observed shift towards lower frequency may be due to hydrogen bonding or increased resonances. Silver and Bovkin¹⁷, have also made the similar observations. In these nickel(II) complexes, we observe this band in the region 1639–1626 cm^{-1} . The shift towards the lower frequency may be interpreted as a consequence of coordination of C=O group to the nickel(II) through oxygen. This results in the lowering of the bond order. A high intensity band observed in the region 1625–1595 cm^{-1} , both in the ligands and the complexes is ascribed to the ethylenic double bond conjugated to the aromatic system in view of the previous assignments^{16, 18}. The medium to high intensity bands appearing in the region 1580–1460 cm^{-1} are assigned to the aromatic C=C stretching vibrations.

The high intensity band in the region 1280–1265 cm^{-1} is attributed to the phenolic C–O vibration in view of the previous assignments¹⁹. In the complexes this band is found in the region 1325–1295 cm^{-1} . This proves that the hydroxy groups are involved in the bond formation.

With the help of magnetic, electronic and infrared spectral data it may be suggested that nickel(II) has coordination number four in these complexes. The construction of the model for the complexes indicates that the monomeric structure involves much steric hindrance as the ligand molecule has to attach itself to the one and the same metal ion through all its coordinating sites. The low solubility of the complexes in the common organic solvents makes one to suggest an extended polymeric chain structure rather than a monomeric or dimeric structure.

In view of these observations we propose the following extended polymeric structure for the complexes in

TABLE II. Infrared Frequencies (in cm^{-1}) of Chalkones and Their Assignments.^a

Assignments	2,2'-di-hydroxy-5'-Me-chalkone	2,2'-di-hydroxy-5,5'-di-Me-chalkone	2,2'-di-hydroxy-5'-Cl-chalkone	2,2'-di-hydroxy-5,5'-di-Cl-chalkone	2,2'-di-hydroxy-5-Me-5'-Cl-chalkone	2,2'-di-hydroxy-5-Cl-5'-Me-chalkone	2,2'-di-hydroxy-5,6-benzo-5'-Cl-chalkone	2-OMe-2'-OH-5'-Cl-chalkone
1. Intermolecular H-bonded -OH stretching vibration =CH and aromatic CH stretching vibration	3200 m 2950 s	3300 m 2900 s	3300 m 2880 s	3280 m 2900 s	3250 m 2950 s	3200 m, br 2900 s	3250 m, br 2900 s	- 2874 s
3. Intramolecular H-bonded -OH stretching vibration	2650 w, br	2675 w, br	2675 w, br	2650 w, br	2675 w, br	2650 w, br	2650 w, br	2667 w, br 2650 w, br
4. C=O stretching vibration	1640 s	1646 s	1650 s	1646 s	1648 s	1648 s	1650 s	1637 m 1639 s
5. Ethylenic C=C stretching vibration	1595 m	1600 m	1600 m	1580 s	1625 m	1600 s	1600 m	1618 m, br -
6. Aromatic C=C stretching vibration	1570 s 1495 m 1480 s	1575 s 1500 m 1470 s	1575 sh 1550 s 1470 s	1570 m -	1575 s 1525 w 1470 s	1558 s -	- 1525 w 1470 s	1575 s 1486 sh 1456 s 1520 sh 1455 s
7. Phenolic C-O stretching vibration	1265 s	1275 s	1280 m	1286 s	1280 s, br	1290 s	1290 m	- 1287 m

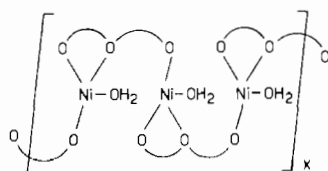
^a m = medium; s = strong; w = weak; br = broad; sh = shoulder.

TABLE III. Infrared Frequencies (in cm^{-1}) of Nickel(II) Chalkonates and Their Assignments.^a

Assignments	Ni(2,2'-di-hydroxy-5'-Me-chalkonate)	Ni(2,2'-di-hydroxy-5'-Cl-5,5'-di-Me-chalkonate)	Ni(2,2'-di-hydroxy-5'-Cl-5-Me,5'-Cl-chalkonate)	Ni(2,2'-di-hydroxy-5'-Cl,5'-Me-chalkonate)	Ni(2,2'-di-hydroxy-5,6-benzo-5'-Me-chalkonate)	Ni(2,2'-di-hydroxy-5,6-benzo-5'-Cl-chalkonate)
1. Intermolecular H-bonded -OH stretching vibration	-	-	-	-	-	-
2. =CH and aromatic CH stretching vibration	2941 m	2941 m	3030 m	2941 m	2940 m	2900 m
3. Intramolecular H-bonded -OH stretching vibration	-	-	-	-	-	-
4. C=O stretching vibration	1626 s	1639 s	1626 s	1626 s	1626 s	1613 s
5. Ethylenic C=C stretching vibration	-	-	1600 m	1600 sh	-	1613 s
6. Aromatic C=C stretching vibration	1550 m 1515 m	1562 s	1575 s 1515 w	1562 m	1562 m 1550 m	1550 m 1538 m
7. Phenolic C-O stretching vibration	1460 m 1325 m	1471 m 1333 m	1460 m 1333 m	1471 s, br 1316 m	1460 s	1471 s 1370 br, sh 1370 m

^a m = medium; s = strong; w = weak; br = broad; sh = shoulder.

which nickel is maintained at the same coordination number:



XIV

Acknowledgements

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