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Complexes of Nickel(II) with Ethylenediamine and 1,3-Diaminopropane Derivatives of 2,2′-Dihydroxychalkones

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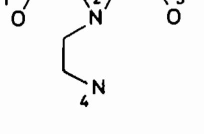
A few complexes of nickel(II) with ethylenediamine and 1,3-diaminopropane derivatives of 2,2′-dihydroxychalkones (L) have been synthesized in ethanol. Analysis shows that the complexes have a 1:1 stoichiometry of the type Ni·L. The involvement of all the active and donor groups has been determined by IR spectroscopy. Magnetic and electronic spectral data suggest a square-planar configuration for the nickel(II) complexes of ethylenediamine derivatives of 2,2′-dihydroxychalkones and these are dimeric in nature, whereas nickel(II) complexes of 1,3-diaminopropane derivatives of 2,2′-dihydroxychalkones have a tetrahedral configuration and are polymeric in nature.

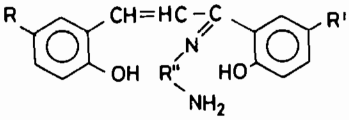
Introduction

The linear tetradentate Schiff bases containing NNNN, ONNO and SNNS donor sequences have been evaluated for complexing abilities and as such the complexes have been thoroughly studied both spectrochemically and magnetochemically [1]. However, the information on branched tetradentates is limited [2]. Therefore, efforts in our laboratory have been concentrated on the design of a new type of branched tetradentate ligand wherein we maintain the sequence of donor atoms. This has culminated in the synthesis of 2,2′-dihydroxychalkone ethylenediamine and 2,2′-dihydroxychalkone-1,3-diaminopropane derivatives.



In our previous papers on copper(II) [3], oxovanadium(IV) [4], and tin(IV) [5], we have shown that copper(II) and oxovanadium(IV) form dimeric complexes with 2,2′-dihydroxychalkone ethylenediamine derivatives, whereas tin(IV) forms polymeric complexes.

Our strategy is to try these ligands with other transition metals. In this paper we report nickel(II) complexes with the following ligands. The intention at this juncture is to study the impact of lengthening of the hydrocarbon bridge between the nitrogen atoms *2* and *4* of the ligands on the stereochemistry of nickel(II) complexes:



	R	R′	R″
I	H	CH_3	$(CH_2)_2$
II	CH_3	CH_3	$(CH_2)_2$
III	H	Cl	$(CH_2)_2$
IV	CH_3	Cl	$(CH_2)_2$
V	H	CH_3	$(CH_2)_3$
VI	CH_3	CH_3	$(CH_2)_3$
VII	H	Cl	$(CH_2)_3$
VIII	CH_3	Cl	$(CH_2)_3$

Experimental

The chemicals used for synthesizing ligands were of reagent grade. Substituted salicylaldehydes and *o*-hydroxyacetophenones were prepared by published methods [6].

The chalkones were prepared as reported earlier [7] and recrystallised from a mixture of benzene and light petroleum.

2,2′-Dihydroxychalkone and diamine in 1:1 molar proportions were refluxed for about 2 hr in alcoholic medium. The crystalline product which separated on cooling was filtered off and recrystallised from alcohol to give shiny plates.

Synthesis of Complexes

Nickel(II) chloride hexahydrate of Analar grade (BDH) was used for preparing the complexes.

Nickel(II) chloride (0.01 mol) in alcohol was added to an alcoholic solution of the ligand (0.012 mol) followed by 2 g of sodium acetate, and refluxed for 4–5 hr. The complex separated was filtered off,

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washed with a mixture of water and alcohol and then with ether and dried under vacuum over fused calcium chloride.

Analysis

The amount of nickel in the complexes was determined gravimetrically as nickel dimethylglyoximate; nitrogen was estimated by the Kjeldahl method.

Physical Methods

Magnetic moments of the complexes at room temperature were measured with a Gouy balance using a glass tube calibrated with $Hg[Co(SCN)_4]$.

Electronic spectra of a few complexes in Nujol mull were recorded on a DMR spectrophotometer in the region 350–1500 nm. The electronic spectra of all the complexes in DMF were taken with an ELICO CL-24.

Infrared spectra of the ligands and complexes in Nujol mull were recorded on a Perkin-Elmer 257.

Molecular weights were determined cryoscopically using nitrobenzene as solvent.

Results and Discussion

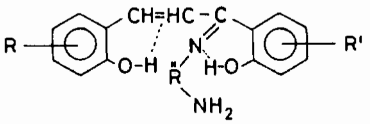
Nature and Stoichiometry

The complexes of the ligands I–IV are reddish brown whereas those of V–VIII are greenish in colour. The complexes I–IV are soluble in common organic solvents, whereas V–VIII are sparingly soluble. The solubility of the complexes in nitrobenzene enabled their molecular weights to be found cryoscopically. The results show the dimeric nature of the complexes (I–IV). Elemental analyses indicate that the complexes conform to a 1:1 stoichiometry of the type Ni·L, where L is a doubly de-protonated ligand (Table I).

Infrared Spectra

The characteristic IR frequencies of the ligands and their complexes are shown in Table II.

The ligands exhibit a broad band of medium intensity in the 3450–3425 cm^{-1} region, which is attributed to the ν(NH) vibration, in analogy with the assignments for aliphatic primary amines [8]. The presence of this band in benzylidene acetophenone-ethylenediamine and benzylidene-acetophenone-1,3-diaminopropane confirms this assignment. The weak broad band with fine structure observed in the region 2730–2580 cm^{-1} are ascribed to the intramolecular hydrogen bonded –OH groups of the following type. Such assignments have been made in the case of salicylidene-*o*-hydroxyaniline [9]. In view of the previous assignment [10, 11] we have assigned a high intensity band found in the region 1640–1630 cm^{-1} to the ethylenic ν(C=C) vibration. The high intensity band due to ν(C=O) present in the region 1650–1640 cm^{-1} disappears in these ligands and a new high intensity band appears in the 1620–1613 cm^{-1} region. This has been assigned to the ν(C=N) vibration. A group of medium to high intensity bands in the region 1583–1484 cm^{-1} is due to the aromatic ν(C=C) vibrations. The high intensity band in the region 1289–1280 cm^{-1} is attributed to the phenolic ν(C–O) vibration. The absence of this band in benzylideneacetophenone-ethylenediame confirms the assignment.



In the complexes, we observe a medium intensity band due to ν(NH) in the region 3375–3300 cm^{-1}; shifting of the band to the lower frequency followed by splitting is evidence for the coordination of $-NH_2$ group to the metal ion. The band due to the intramolecular H-bonded –OH disappears and the phenolic C–O appears as a strong band in the region 1320–1300 cm^{-1}. These observations suggest that the ligands have undergone deprotonation while reacting with nickel(II) chloride, thus forming the complexes of the type NiL. The ν(C=N) vibration in

TABLE I. Elemental Analyses, Molecular Weights and Magnetic Moments of Nickel(II) Complexes.

Complex No.	Ligand No.	Empirical Formula	Molecular Wt.		Ni%		N%		μ_{eff} (in B.M.)
			Calcd.	Found	Calcd.	Found	Calcd.	Found	
1	I	$(C_{18}H_{18}N_2O_2)Ni$	352.7	731.0	16.64	16.23	7.93	7.82	Diamagnetic
2	II	$(C_{19}H_{20}N_2O_2)Ni$	366.7	682.0	16.00	15.98	7.63	7.52	Diamagnetic
3	III	$(C_{17}H_{15}N_2O_2Cl)Ni$	373.2	694.0	15.72	15.60	7.50	7.32	Diamagnetic
4	IV	$(C_{18}H_{17}N_2O_2Cl)Ni$	387.2	789.0	15.16	15.30	7.23	7.20	Diamagnetic
5	V	$(C_{19}H_{20}N_2O_2)Ni$	366.7	*	16.00	16.23	7.63	7.48	4.48
6	VI	$(C_{20}H_{22}N_2O_2)Ni$	380.7	*	15.41	14.90	7.35	7.20	4.49
7	VII	$(C_{18}H_{17}N_2O_2Cl)Ni$	387.2	*	15.16	15.10	7.23	7.35	4.43
8	VIII	$(C_{19}H_{19}N_2O_2Cl)Ni$	401.2	*	14.63	14.82	6.97	7.25	4.46

*The complexes are not soluble enough to enable the molecular weight determination.

TABLE II. Important Infrared Frequencies (in cm^{-1}) of Nickel(II) Complexes and Their Assignments.

Comp	ν(NH)	ν(C=C) Ethylenic	ν(C=N)	ν(C=C) Aromatic	ν(C–O) Phenolic	ν(Ni–N) + ν(Ligand)	ν(Ni–N)	ν(Ni–O) + ν(Ligand)	ν(Ni–O)
1	3300brm	1630s	1600s	1560brm 1530m	1300s	–	–	–	–
2	3350brm	1630s	1580s	1540s –	1330s	530s 470s	380m	410s 270m	300m
3	3375brm	1620s	1605m	1580m 1540w 1520m	1320s	520brm 450m	370m	420s 260m	295m
4	3350brm	1630s	1680s	1540s 1520s	1320s	–	–	–	–
5	3350brm	1620s	1600s	1580s 1540s	1310s	530brs 460s	360brm	425brm 260m	310m
6	3350brm	1635s	1600s	1560s 1500sh	1320s	530s 500w 470s	380m	410s 270m	300m
7	3350brm	1620s	1600m	1580s 1500s	1310s	–	–	–	–
8	3350brm	1635s	1600s	1560s 1500m	1320s	510s 460s	365m	410m 255m	310m

the complexes appears as a medium to high intensity band in the region 1605–1580 cm^{-1}. The shifting of ν(C=N) to lower frequency relative to the ligands indicates that the –C=N group is coordinated to the metal ion through nitrogen.

The ν(M–N) vibrations assigned in the region 600–500 cm^{-1} are found to be insensitive to the metal ion [12]. The metal-sensitive vibrations are reported to occur in lower frequency region [13]. For Cu(II) and Ni(II) complexes of glycine, these bands are located in the regions 483–442 and 337–289 cm^{-1}. These assignments are founded on the ^{14}N–^{15}N isotopic studies [14]. For Ni(II) complexes of quadridentate Schiff bases, partially sensitive bands at 533 and 448 cm^{-1} are assigned as ν(Ni–N) vibrations coupled with ligand vibrations. The isotope sensitive bands appearing at 432 and 365 cm^{-1} are considered to be due to ν(Ni–N) vibrations [15]. In view of these assignments we assign bands in the regions 530–510 and 470–450 cm^{-1} to the ν(Ni–N) vibration coupled with ligand vibration. The medium intensity band in the region 380–360 cm^{-1} is regarded as due to the ν(Ni–N) vibration.

For the transition metal acetylacetonates the ν(M–O) vibrations are located in the region between 500 and 400 cm^{-1} [13, 16]. Percy [17] has studied Ni(II) Schiff base complexes using ^{16}O, and has assigned isotope-sensitive bands at 323 and 294 cm^{-1} to ν(Ni–O) vibrations. Partially isotope sensitive bands found at 348 and 246 cm^{-1}, were assigned to ν(Ni–O) + ν ligand vibrations [14]. Thus in these nickel(II) complexes, we regard the bands in the regions 425–410 and 270–255 cm^{-1} as due to ν(Ni–O) vibrations associated with ligand vibrations. The medium intensity band in the region 310–295 cm^{-1} is attributed to the ν(Ni–O) vibration.

Magnetic Data

All the nickel(II) complexes of the ligands I–IV are diamagnetic, indicating that nickel(II) in these complexes has a square-planar configuration. The magnetic moments obtained for nickel(II) complexes of ligands V–VIII are in the range of 4.43–4.49 B.M. Theory predicts that, because of the high orbital contribution to the magnetic moments, the nickel(II) tetrahedral complexes exhibit moments in the range of 3.5 to 4.2 B.M. [18]. It may, therefore, be concluded that nickel(II) has a tetrahedral environment in these complexes.

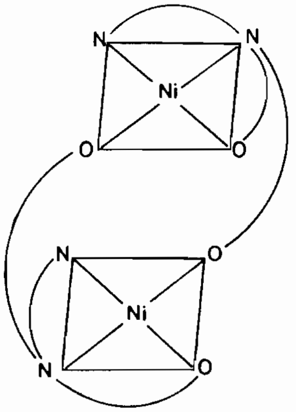
Electronic Spectra

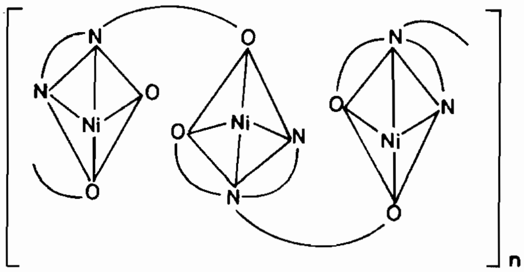
The complexes of nickel(II) having square planar configuration are commonly orange or red in colour [19, 20]. However, examples of purple and green are also known in the literature. These complexes exhibit a broad band in the region 15 000–23 000 cm^{-1} with a second band in the range of 23 000–27 000 cm^{-1}. These bands are assigned to the transitions $^1A_{1g} \rightarrow {}^1A_{2g}$ and $^1A_{1g} \rightarrow {}^1B_{1g}$. Often the second band is overlaid by the high intensity charge-transfer band, and hence the band 15 000–23 000 cm^{-1} is taken as a characteristic band for square-planar complexes.

In these Ni(II) complexes of ligands I–IV, we observe a broad band in the region 16 000–17 395 cm^{-1} and this may be attributed to the transition $^1A_{1g} \rightarrow {}^1A_{2g}$. The band due to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition appears in the region 21 276–22 727 cm^{-1}. This band has high intensity and may be due to the overlaying M–L charge transfer band. These observations suggest that these Ni(II) complexes of ligands I–IV have square planar configuration.

The complexes of ligands V–VIII have different spectra; these display two bands in the region of 16 129–13 889 cm^{-1}. It is documented in the literature that tetrahedral nickel(II) complexes show high intensity bands in the regions 16 667–14 286 and 8 000–7 143 cm^{-1} [18–20]. The observed high intensity of the band in the region 16 129–13 889 cm^{-1} and the absence of the band around 25 000 cm^{-1} have made it obvious that nickel(II) in these complexes has a tetrahedral configuration. The high intensity band observed in the above region is attributed to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition.

With the help of i.r., electronic spectra and magnetic data it may be suggested that nickel(II) has the coordination number four in these complexes. The complexes of the ligands I–IV are diamagnetic and dimeric in nature, hence they have square-planar configuration. The complexes of ligands V–VIII display magnetic moments agreeing with tetrahedral configuration. The electronic spectra also support this conclusion. The insolubility of these complexes in various solvents suggests that these may be polymers. The construction of models for these complexes suggests that O(3), N(2) and N(4) can form bonds with one and the same metal ion without any steric hindrance. As O(1) has been separated by the ethylenic hydrocarbon bridge, it cannot form a bond with the same metal ion. Thus it forms bond with another metal moiety giving rise to a dimer or a polymeric chain. It is evident that the lengthening of the hydrocarbon bridge between the nitrogen atoms N(2) and N(4) drifts the Nickel(II) complex from dimeric to polymeric, and alters the configuration from square-planar to tetrahedral.





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