

Spin state variation in nickel(II) complexes of a redox-active Schiff base

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Summary

Nickel(II) complexes of a redox-active tetradentate Schiff base ligand with ethylene/propylene linkages have been prepared and characterized by spectroscopic and magnetic studies. The complexes are diamagnetic in the solid state and exhibit paramagnetic behaviour in solution. Reflectance spectra of the samples indicate a shift of the main d–d band envelope to lower energies as the bridge is changed from ethylene to propylene.

Introduction

Mixed nitrogen–oxygen ligands have been the subject of much interest and Schiff bases, in particular, have been studied extensively⁽¹⁾. A variety of new methods have been used to prepare nickel(II) complexes of tetradentate Schiff bases; these include the preparation of the ligand prior to complexation of a suitable α -hydroxyaldehyde with a diamine^(2–7), the use of template reactions⁽⁸⁾ and *in situ* reactions^(9,10). Although O_3N , O_2N_2 and ON_3 donor sets are possible, the most common tetradentate donor set is N_2O_2 ^(2,11). A wide range of Schiff-base ligand complexes of nickel(II) incorporating O_2N_2 ^(12–17) donor sets have been prepared. The crystal structures of nickel(II) complexes with the ligands derived from O-methoxy-phenylene diamine have been reported by Casellato⁽¹⁸⁾. Recently Fujiwara *et al.*⁽¹⁹⁾ have extended their work to nickel(II) Schiff-base complexes having N_2O_2 donor sets. The ligand systems contain the 2-methylbutyl or 2-methylphenyl group and their benzoyl derivatives are characterized by ¹H- and ¹³C-n.m.r. spectroscopy.

With these facts in mind, tetradentate Schiff bases utilizing 2,5-dihydroxyacetophenone with 1,2-ethanediamine and 1,3-propanediamine were prepared, providing a square planar site for binding the nickel(II) ion with an additional redox-active site.

Experimental

All chemicals (A.R. grade) were used without further purification.

Preparation of DAen and DApn

2,5-Dihydroxyacetophenone was prepared by Fries Rearrangement of hydroquinone diacetate⁽²⁰⁾. The Schiff bases were prepared by heating 2,5-dihydroxyacetophenone and 1,2-ethanediamine/1,3-propanediamine (2:1) under reflux in EtOH for 1 h. The solution was filtered hot and the filtrate was cooled at ca 4 °C, whereupon an orange product precipitated. DAen (Found: C, 65.4; H, 6.8; N, 9.0; $C_{18}H_{20}N_2O_4$ calcd.: C, 65.8; H, 6.1; N, 8.5%). ¹H-n.m.r. (DMSO-*d*₆): 2.55(s, 6H); 4.15(s, 4H); 6.85–7.15(m, 4H); 7.35(d, 2H); 9.15(s, 2H); 10.2(s, 2H). DApn (Found: C, 66.4; H, 6.7; N, 8.0; $C_{19}H_{22}N_2O_4$ calcd.: C, 66.6; H, 6.4; N,

8.2%). ¹H-n.m.r. (DMSO-*d*₆): 1.50(s, 2H); 2.5(s, 6H); 4.10(t, 4H); 6.8–7.4(m, 6H); 9.15(s, 2H); 10.1(s, 2H).

Preparation of $Ni(L)X_2 \cdot nH_2O/EtOH$ ($L = DAen$ and $DApn$; $X = Cl^-$ or NO_3^-)

Ligand L (1 mmol) was suspended in EtOH (10 cm³) and a $NiCl_2/Ni(NO_3)_2$ (1.2 mmol) solution in EtOH (5 cm³) added to the suspension; the mixture was stirred for 30 min at room temperature. At this point the solution was filtered, and the filtrate restirred for 3.5 h, whereupon brown products formed. These were centrifuged, washed with EtOH and Et₂O, and dried over P_4O_{10} . $[Ni(DAen)]Cl_2 \cdot 4H_2O$: (Found: C, 41.0; H, 5.0; N, 5.5; Ni, 11.6; $C_{18}H_{28}N_2O_8Cl_2Ni$ calcd.: C, 40.8; H, 5.3; Ni, 11.1%). $[Ni(DApn)]Cl_2 \cdot 2H_2O$: (Found: C, 44.5; H, 5.3; N, 5.8; Ni, 12.0; $C_{19}N_2O_6Cl_2Ni$ calcd.: C, 44.9; H, 5.1; N, 5.5; Ni, 11.6%). $[Ni(DAen)](NO_3)_2 \cdot 2EtOH$: (Found: C, 43.0; H, 5.7; N, 9.6; Ni, 9.5; $C_{22}H_{32}N_4O_{12}Ni$ calcd.: C, 43.8; H, 5.3; N, 9.3; Ni, 9.7%). $[Ni(DApn)](NO_3)_2$: (Found: C, 43.8; H, 4.4; N, 10.2; Ni, 11.5; $C_{19}H_{22}N_4O_{10}Ni$ calcd.: C, 43.5; H, 4.2; N, 10.7; Ni, 11.2%).

Preparation of $[Ni(L)(OAc)_2] \cdot nH_2O$ ($L = DAen$ and $DApn$)

Ligand L (1 mmol), suspended in EtOH (10 cm³), was added to a solution of $Ni(OAc)_2$ (1.2 mmol) in EtOH (10 cm³). The mixture was stirred for 4 h at room temperature and the resulting brown products were centrifuged, washed with EtOH and Et₂O, and dried over P_4O_{10} . $[Ni(DAen)(OAc)_2] \cdot H_2O$: (Found: C, 51.2; H, 5.16; N, 5.2; Ni, 10.7; $C_{22}H_{26}N_2O_7Ni$ calcd.: C, 50.4; H, 5.03; N, 5.3; Ni, 11.2%). $[Ni(DApn)(OAc)_2]$: (Found: C, 53.5; H, 5.4; N, 5.8; Ni, 11.6; $C_{23}H_{28}N_2O_6Ni$ calcd.: C, 53.2; H, 5.4; N, 5.4; Ni, 11.3%).

Preparation of $[Ni(DAen)](SCN)_2 \cdot 4H_2O$

The ligand (1 mmol) was suspended in EtOH (10 cm³). A solution of $NiCl_2$ (1.2 mmol) in 10 cm³ of EtOH was mixed with an EtOH saturated solution of KCNS. The precipitated KCl was removed by filtration and the ligand suspension was added to the filtrate. The reaction mixture was stirred for 4 h at room temperature and the dark brown products were centrifuged, washed with EtOH and Et₂O, and dried over P_4O_{10} . $[Ni(DAen)](SCN)_2 \cdot 4H_2O$: (Found: C, 41.5; H, 4.4; N, 9.4; Ni, 10.8; $C_{20}H_{28}N_4O_8S_2Ni$ calcd.: C, 41.8; H, 4.9; N, 9.7; Ni, 10.8%).

Measurements

C, H, N were analysed microanalytically at the University of Delhi (USIC). Nickel was estimated by AAS. Electronic spectra were recorded on a Perkin-Elmer 554 spectrometer. ¹H-n.m.r. spectra were recorded on 90 MHz Perkin-Elmer R-32 spectrometer. I.r. spectra were taken on a Shimadzu IR-435 spectrometer in Nujol mull. Magnetic

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susceptibility data were obtained using a Cahn 2000 magnetic balance. Diamagnetic corrections were made using Pascal's constant.

Results and discussion

Magnetic susceptibility

The magnetic susceptibilities of the complexes are given in Table 2. They are diamagnetic at room temperature, except for the acetato complexes which are weakly paramagnetic in the solid state.

An early compilation⁽²¹⁾ of magnetic moment data of nickel(II) complexes, plus more recent observations, reveal that all NiO₄-type complexes are paramagnetic, whereas Ni-S₄ and Ni-S₂N₂ complexes are diamagnetic (in the absence of steric strain). With Ni-O₂N₂ complexes there is a distribution, by far most prevalent in the latter case, between spin-paired and spin-free forms depending upon the specific nature of ligand donor within a class, and the additional factors of solvent and temperature⁽²²⁾. The O₂N₂ case at this time seems particularly representative of the intermediate situation in which the ligand field strength may or may not be sufficient to pair spins⁽²³⁾. In the present series of complexes the average ligand field is such that it is quite near the magnetic cross-over point. The introduction of a weak tetragonal Z component is sufficient to decrease the singlet-triplet separation. This may be the reason for the acetato complexes being paramagnetic. For the series with the ethylene chain, solution susceptibility of the complexes in DMSO-d₆ was obtained using Evan's method⁽²⁴⁾. The solution susceptibility data show the complexes to be paramagnetic. μ_{eff} data incorporating the diamagnetic corrections are given in Table 2, which reveals a typical high spin nickel(II) ion configuration. Owing to the limited solubility of these complexes in non-coordinating solvents it was not possible to evaluate their magnetic character in non-polar solvents.

The theoretical μ_{eff} has been calculated using the Dq and B values, and it is found that they are similar to the experimental solution susceptibility data. In conclusion, the complexes are diamagnetic in the solid state, except the acetato complexes, and in solution they exhibit paramagnetic behaviour.

Reflectance spectra

Visible spectra of the complexes in the solid state exhibit a broad band in the 500–600 nm region; two representative examples are shown in Figure 1. Diamagnetic nickel(II) complexes in C_{2v} symmetry exhibit only one spin-allowed band in the 500–700 nm region, which has been assigned as the $^1A_1(F) \rightarrow ^1B_1(G)$ transition⁽²⁵⁾. The present series of complexes show that the band ranges between 520 and 545 nm for the ethylene linker and 540–560 nm for the propylene linker. Comparing the ethylene and propylene linker nickel(II) complexes it was found that the ligand field strength decreases as the bridge length increases (Table 1).

Absorption spectra

The u.v. spectra of nickel(II) complexes show characteristic absorption bands for the Schiff-base group. Absorption maxima and respective extinction coefficients are reported in Table 2.

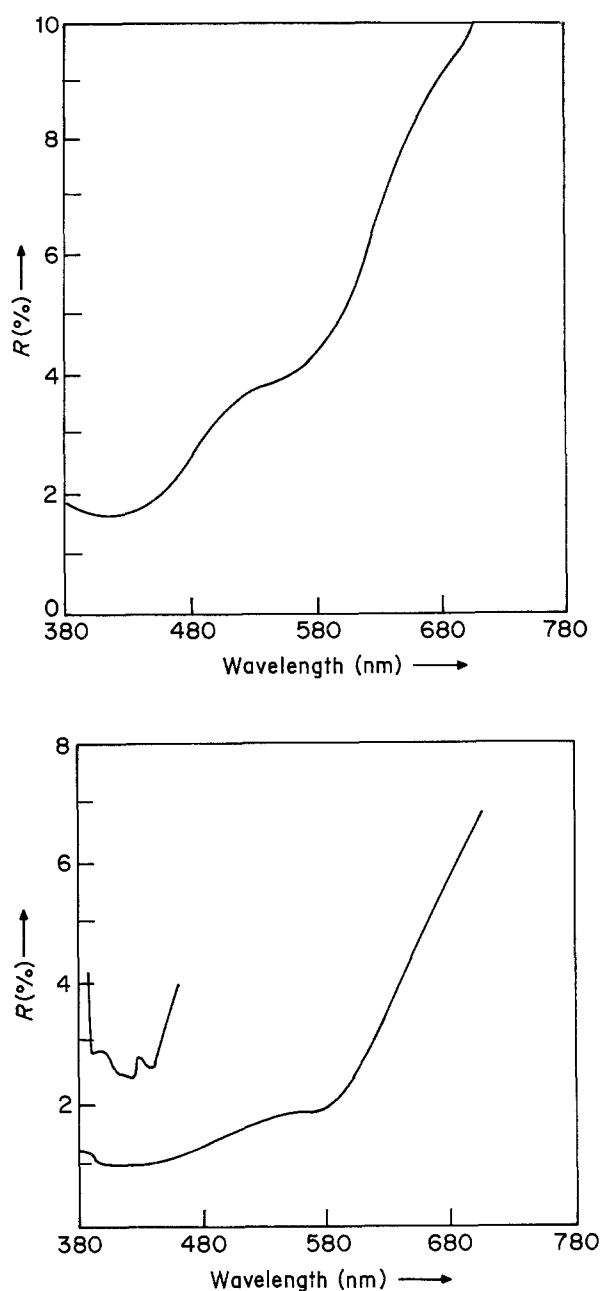


Figure 1. (a) Reflectance spectra of Ni(DAen)Cl₂·4H₂O in the 380–700 nm range; (b) reflectance spectra of Ni(DApn)Cl₂·2H₂O in the 380–700 nm range.

The present series of complexes show typical bands in the near u.v.–vis. region. Since the electronic spectra indicate a high energy band in a region $> 25000 \text{ cm}^{-1}$ this suggests that the nickel(II) complexes are six-coordinate in solution, most likely with two axially-bound solvent molecules, a result that supports the high-spin data for nickel(II) in DMSO-d₆.

Assignment of spectral results

The assignment of the $^3A_{2g} \rightarrow ^3T_{2g}(F)$ transition to the band at $ca 9000\text{--}11000 \text{ cm}^{-1}$ is reasonable, as $10Dq$ for related Schiff-base nickel(II) complexes lies in the 10500 cm^{-1} range. The value for the above transition has been calculated using the ratio of frequencies for the transitions observed at $ca 29000$ and 18000 cm^{-1} for each complex, together with data recorded by Lever⁽²⁵⁾. The next band observed appears in the $17467\text{--}18691 \text{ cm}^{-1}$

Table 1. Reflectance and magnetic data for the nickel(II) complexes

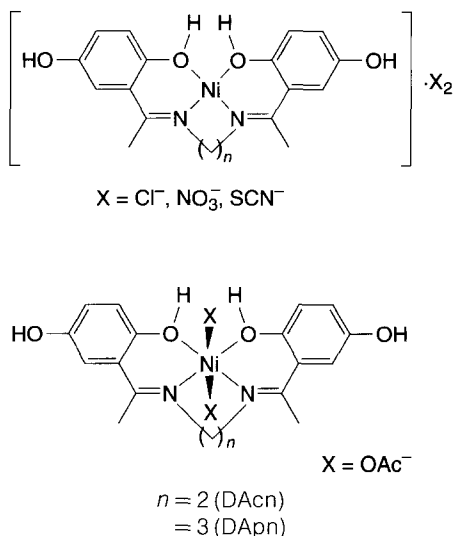
Complex	λ_{\max} (nm)	μ_{eff} (solid)
[Ni(DAen)]Cl ₂ ·4H ₂ O	525	Diamag.
[Ni(DAen)(OAc) ₂]·H ₂ O	530	2.83
[Ni(DAen)](SCN) ₂ ·4H ₂ O	520	Diamag.
[Ni(DAen)](NO ₃) ₂ ·2EtOH	545	Diamag.
[Ni(DApn)]Cl ₂ ·2H ₂ O	560	Diamag.
[Ni(DApn)(OAc) ₂]	540	3.40
[Ni(DApn)](NO ₃) ₂	555	Diamag.

Table 2. Observed optical bands with their extinction coefficients and magnetic moments of nickel(II) complexes in DMSO

Complex	λ_{\max} (nm)	log ϵ	μ_{eff} (sol.) ^a
[Ni(DAen)]Cl ₂ ·4H ₂ O	332	3.90	3.63
	348	3.80	
	435	4.12	
	570	2.55	
[Ni(DAen)(OAc) ₂]·H ₂ O	328	3.77	3.10
	354	3.77	
	432	3.96	
	565	2.83	
[Ni(DAen)](SCN) ₂ ·4H ₂ O	336	3.80	3.38
	354	3.95	
	430	3.79	
	560	2.55	
[Ni(DAen)](NO ₃) ₂ ·2EtOH	326	4.05	3.25
	356	4.05	
	435	4.06	
	572	2.77	
[Ni(DApn)]Cl ₂ ·2H ₂ O	330	3.70	–
	350	3.75	
	424	3.60	
	572	2.77	
[Ni(DApn)(OAc) ₂]	326	3.80	–
	354	3.72	
	427	3.95	
	572	2.77	
[Ni(DApn)](NO ₃) ₂	332	3.85	–
	348	3.70	
	427	3.82	
	572	2.77	

^aEvan's method.

region and is assigned to the ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{F})$ transition. The next higher energy band observed in these complexes occurs in the 30674–29761 cm^{−1} region and these are assigned to the ${}^3B_{1g} \rightarrow {}^3A_{2g}({}^3P)$, ${}^3B_{1g} \rightarrow {}^3E_g({}^3P)$ transitions. Table 2 incorporates the Dq and B values as obtained by the method of Lever⁽²⁵⁾, using the equation: $\nu_3 + \nu_2 = 30Dq + 15B$. The theoretical value of the middle band has been calculated, and comparison with experimental values shows that they are similar, suggesting that the Dq and B values are good approximations, within experimental error. Presence of a high energy band at $\lambda_{\max} > 25000 \text{ cm}^{-1}$ and the Dq value of nickel(II) complexes favours a six-coordinate rather than a four-coordinate square planar or tetrahedral complex. Moreover, the rigidity of these ligands does not allow departure of symmetry to a degree greater than D_{2d} ⁽²⁶⁾. The above evidence thus rules out the presence of T_d , high-spin complex in solution.

**Figure 2.** Proposed structures of the nickel(II) complexes.

I.r. spectroscopy

In the i.r. spectra of the free ligands a strong band appears in the 1600–1620 cm^{−1} region. On the basis of an analogy with the assigned bands for the Schiff-base group, the 1600 cm^{−1} band is attributed to $\nu(\text{C}=\text{N})$. In the present series of nickel(II) complexes a 20–35 cm^{−1} shift is observed, implying direct coordination of imine nitrogen atoms to the metal centre. The band at ca 2900 cm^{−1} also shifts 30–50 cm^{−1} upon coordination.

In [Ni(DAen)(OAc)₂]·H₂O and [Ni(DApn)(OAc)₂] complexes new bands are observed at 1340 and 1560, and 1320 and 1540 cm^{−1}, respectively, commensurate with the unidentate binding mode of the acetate group to the metal centre. In [Ni(DAen)](NO₃)₂·2EtOH and [Ni(DApn)](NO₃)₂ complexes a strong band is observed at ca 1775 and 1750 cm^{−1}, respectively, and may be due to a free nitrate group. A strong band at ca 2050 cm^{−1} may be ascribed to the free thiocyanate group. Thus, the presence of anions, such as NO₃[−] and OAc[−], in the complexes have been confirmed by i.r. data, while the presence of Cl[−] was confirmed chemically. The proposed structures of the complexes, given in Figure 2, are based upon the above data.

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TMC 3297