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Syntheses and Solution Equilibria of Nickel(II) Chelates. II. Dinuclear Mixed Ligand Species[1]

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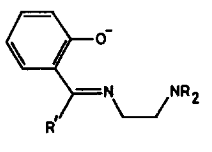
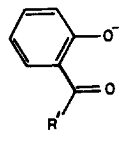
A new class of mixed ligand complexes of nickel(II) are reported. They have the stoichiometry LKNi where L is a potentially tridentate Schiff base anion and K is the corresponding bidentate carbonyl species. The complexes show clearly defined C=O and C=N stretches in the infrared. Where solubility permitted the determination of molecular weights, the compounds were found to be dimeric in freezing benzene and/or bromoform. The complexes are uniformly high-spin and have magnetic moments in the range 3.0-3.2 BM. On the basis of electronic spectral data it is concluded that the compounds have, in general, pseudooctahedral environment around each nickel(II) in the solid state. In one case the environment is believed to be square pyramidal. Structures which accommodate these geometrical requirements are suggested within the dimeric framework. Solution spectra are solvent and temperature dependent. The results are interpreted in terms of equilibria involving the two geometries. The possible occurrence of monomeric species at low concentration is examined.

Introduction

The bis complexes of nickel(II) derived from the potentially tridentate salicylaldimine ligands, 1a, show[2] interesting stereochemical properties in the solid state and in solution. In view of our interest[1] in the complexes of Schiff bases derived from 2-hydroxyaryl carconyl compounds, we attempted the synthesis of the complexes of the ligands 1b and 1c using a non-aqueous chelation reaction.[1] Quite unexpectedly, this led to the discovery of a hitherto unknown class of mixed-ligand complexes of nickel(II). The syntheses and some general properties of these unusual species are described in this paper.[3]



1a: $R'=H$; salNR$_2$
1b: $R'=CH_3$; hacNR$_2$
1c: $R'=C_2H_5$; hprNR$_2$



2a: $R'=H$; sal
2b: $R'=CH_3$; hac
2c: $R'=C_2H_5$; hpr

R = alkyl group

Results

Synthesis and Characterisation. The anion (1b or 1c) of the Schiff base generated by the addition of potassium *t*-butoxide to the base in dry tetrahydrofuran is found to react with $(Et_4N)_2(NiBr_4)$. From the reaction mixture only one kind of complex can be isolated. This has the stoichiometry LKNi where L stands for 1b or 1c and K stands for the anion (2b or 2c) of the corresponding carbonyl compound. For example, when HhacNR$_2$ is the Schiff base, the complex obtained has the composition, (hacNR$_2$)(hac)Ni. The above synthetic procedure failed to give rise to the bis complex, L$_2$Ni. However, by reacting K$_2$Ni xH$_2$O with N,N-dialkylethylenediamine in the molar ratio 1:2 in boiling toluene, the bis complex can be obtained in good yield. (These bis complexes will not be described in this paper). More important is the observation that the same reaction carried out in the molar ratio 1:1 raidly gives rise to the mixed ligand complex LKNi. This provides a simple and ready method for the synthesis of LKNi complexes.

The bis salicylaldimine complexes, (salNR$_2$)$_2$Ni, were described[2] by Sacconi *et al.* several years ago. We now report that the mixed ligand complex (salNR$_2$)(sal)Ni is stable and is kinetically accessible by a variety of routes: (i) reaction of (sal)$_2$Ni . 2H$_2$O with N,N-dialkylethylenediamine; (ii) reaction of (sal)$_2$Ni . 2H$_2$O with (salNR$_2$)$_2$Ni; (iii) reaction of (salNR$_2$)$_2$Ni with salicylaldehyde. In each case the reactants are taken in the molar ratio 1:1 in either ethanol or toluene. The most efficient synthesis is achieved using route (i) in toluene.

Analytical data of a few selected mixed ligand complexes are shown in Table I. The compounds are generally green in colour. The complex (salNEt$_2$)-(sal)Ni is obtained as a green dihydrate which readily loses water giving the brown anhydrous compound. The chelates are more or less soluble in a variety of organic solvents. The solubility is highest for the (salNR$_2$)(sal)Ni complexes and it increases with the size of the R group.

Molecular Weights. Only in a few cases are the

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(1) Part 1, T.S. Kannen and A. Chakravorty, *Inorg. Chem.*, *9*, 1153 (1970).
(2) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, *4*, 943 (1965).
(3) Preliminary communication: T.S. Kannan and A. Chakravorty, *Inorg. Nucl. Chem. Letters*, *6*, 903 (1970).

Table I. Characterization data of mixed ligand complexes.

Compound	Formula	MP °C[a]	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found
(salNMe$_2$)(sal)Ni	$C_{18}H_{20}N_2O_3Ni$	248-250	58.26	57.72	5.43	5.38	7.55	7.54
(hacNMe$_2$)(hac)Ni [b]	$C_{20}H_{24}N_2O_3Ni$	199-200	60.18	60.22	6.06	6.22	7.02	6.87
(hprNMe$_2$)(hpr)Ni	$C_{22}H_{28}N_2O_3Ni$	178-179	61.85	61.77	6.61	6.63	6.56	6.74
(salNEt$_2$)(sal)Ni [c,b]	$C_{20}H_{24}N_2O_3Ni$	92-93	60.18	60.24	6.06	6.30	7.02	7.14
(hacNEt$_2$)(hac)Ni	$C_{22}H_{28}N_2O_3Ni$	206-207	61.85	61.82	6.61	6.90	6.56	6.54
(salNBu$_2$)(sal)Ni [e,f]	$C_{24}H_{32}N_2O_3Ni$	97-98	63.32	61.90	7.08	7.13	6.15	6.14

[a] All melting points are uncorrected. [b] Nickel was estimated as the dimethylgloximate; % Ni, Calcd., 14.71; Found, 14.50. [c] % Ni, Calcd., 14.71; Found, 14.95. [d] This complex forms a dihydrate which loses water in vaccum, % H_2O, Calcd., 8.27, Found, 9.00. [e] % Ni, Calcd., 12.90, Found, 12.20. [f] This compound is difficult to purify and the sample, may be slightly impure.

Table II. Molecular Weight Data.

Compound	Solvent	Concentration (*M*)	Molecular weight Observed	Molecular weight Calculated (dimer)
(salNEt$_2$)(sal)Ni	benzene	0.0197	738	798
		0.0244	767	798
	bromoform	0.0279	780	798
		0.0301	791	798
(hacNEt$_2$)(hac)Ni [a]	bromoform	0.0143	800	854
		0.0196	850	854
(salNBu$_2$)(sal)Ni [b]	benzene	0.0110	798	910

[a] Too insoluble in benzene for molecular weight determination in this solvent. [b] This complex is difficult to purify and the sample may be slightly impure (vide Table I).

Table III. Some infrared frequencies (cm^{-1})[a]

Compound	Assignment νC=O	νC=N	νAromatic
(sal)$_2$Ni . 2H$_2$O	1625	—	1600
(hac)$_2$Ni . 2H$_2$O	1623	—	b
(n-Busal)$_2$Ni [c]	—	1612	1595
(hacNMe$_2$)$_2$Ni	—	1590	b
(salNMe$_2$)(sal)Ni	1648	1630	1600
(hacNMe$_2$)(hac)Ni	1623	1600	1582
(hprNMe$_2$)(hpr)Ni	1628	1600	1580
(salNEt$_2$)(sal)Ni	1640	1620	1596
(hacNEt$_2$)(hac)Ni	1617	1600	1587
(salNBu$_2$)(sal)Ni	1640	1625	1603

[a] Measurements were done in KBr disc and also in carbon tetrachloride (where solubility permitted); the spectra remained invariant in the two media. [b] Not clearly resolved. [c] Bis(*n*-butyl salicylaldiminato)nickel(II).

Table IV. Magnetic moments (BM) of complexes.

Compound	Temperature °C	Moment (solid)
(salNMe$_2$(sal)Ni [a]	25	3.12
(hacNMe$_2$)(hac)Ni	25	3.12
(hprNMe$_2$)(hpr)Ni	25	3.11
(salNEt$_2$)(sal)Ni [b,c]	28	3.00
(hacNEt$_2$)(hac)Ni [d]	27	3.26
(salNBu$_2$)(sal)Ni	28	3.12

[a] Solution moments in chloroform: 28°, 311; 40°, 3.15 and 56°, 3.15 BM. [b] Solution moments in toluene, 28°, 3.00; 45°, 3.05; 59°, 3.05 and 72°, 3.05 BM. [c] Solution moment in chloroform, 21°, 3.12 BM. [d] Solution moment in chloroform, 21°, 3.12 BM and in toluene, 21°, 3.20 BM.

solubilities high enough for reliable cryoscopic determination of molecular weights (Table II). The observed molecular weights in benzene and bromoform are close to those calculated for the dimer $L_2K_2Ni_2$. This result is of cardinal importance in the rationalization of observed spectral and magnetic properties of the mixed ligand complexes. For brevity we shall continue to represent the complexes as LKNi.

Infrared Spectra. These were studied mainly with the purpose of showing the presence of L and K fragments using C=N and C=O stretches respectively. The results are collected in Table III.

Magnetic Data. All mixed ligand complexes are paramagnetic in the solid state and the room temperature moments lie in the range 3.0-3.2 BM. In the cases examined the magnetic moment did not change significantly on dissolving in toluene, benzene or chloroform. Results are collected in Table IV.

Electronic Spectra. Spectral data in nujol mull are illustrated in Figure 1. Solution spectra (Figures 2-3) are in general dependent on temperature and solvent. Extinction coefficients of bands were calculated using the molarity of nickel(II) and not of the dimer.

Discussion

Synthesis and Formula. In the syntheses in tetrahydrofuran, the mixed ligand complex alone is formed even when carefully purified Schiff base is used. At some stage of the synthesis, part of the Schiff base apparently undergoes hydrolysis to generate the carbonyl compound which acts as a coordinating agent. No particular precautions were taken to exclude atmospheric moisture during the syntheses. The mechanism of the hydrolysis reaction was not investigated.

The mixed ligand complexes generally show three infrared bands in the region 1570-1650 cm^{-1} (Table II). By comparing the results with those of the bis complexes of the type L_2Ni and K_2Ni the three bands can be confidently assigned. The C=O and C=N stretches are clearly observed in each mixed ligand complex and lie in the ranges 1615-1650 cm^{-1} and 1590-1630 cm^{-1} respectively. The third band—observed in most but not all cases—in the region 1580-15600 cm^{-1} is due to aromatic vibration. The systematic presence of C=O and C=N stretches is a necessary condition for the mixed ligand formulation.

A few mixed ligand salicylaldimine-salicylaldehyde complexes are reported in literature. Many years ago Pfeiffer and Krebs reported[4] the synthesis of the green copper(II) complex, $(salNEt_2)(sal)Cu$. This compound is monomeric in solution and is most probably trigonal bipyramidal.[5] A series of mixed ligand oxovanadium(IV) species of the type $(salNR_2)(sal)VO$ are known to be monomeric and pseudooctahedral.[6]

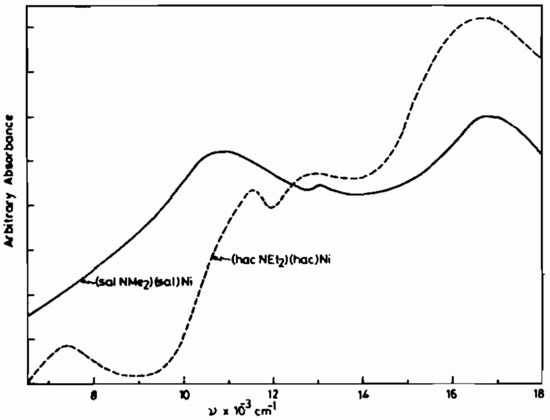


Figure 1. Spectra of $(salNMe_2)(sal)Ni$ and $(hacNEt_2)(hac)Ni$ in nujol (25°C).

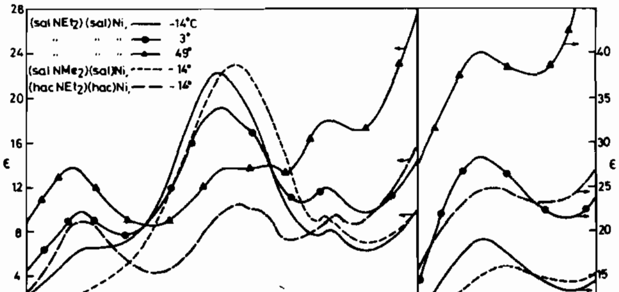


Figure 2. Electronic spectra of $(salNEt_2)(sal)Ni$, $(hacNEt_2)$-$(hac)Ni$ and $(salNMe_2)(sal)Ni$ in chloroform.

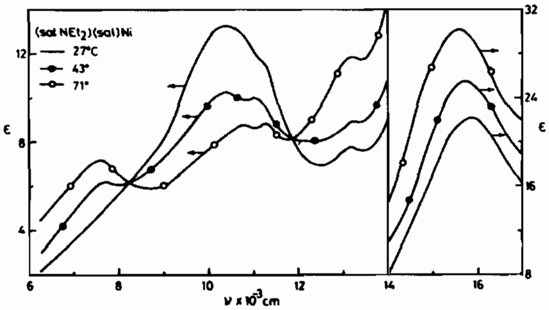
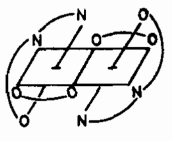


Figure 3. Figure 3. Electronic spectra of $(salNEt_2)(sal)Ni$ in toluene.

Structure in the Solid State. All the mixed ligand complexes are high-spin and have magnetic moments corresponding to two unpaired electrons. In the solid state all the complexes—except $(hacNEt_2)(hac)$-Ni which is discussed later—show three well defined bands (Figure 1) in the visible and near-ir regions. The position and shape of the three bands are suggestive of an effective octahedral geometry around nickel (II). The assignments are: ${}^3A_{2g}\rightarrow{}^3T_{2g}$ (F) ~10,700; $\rightarrow$E(D) ~ 13,300; $\rightarrow{}^3T_{1g}$ (F), ~ 16,400 cm^{-1}.

In view of solution molecular weight data and the general similarity of solution and solid spectral data (*vide infra*) we shall *assume* that the complexes are dimeric in the solid state. Several structures can be written for the dimer satisfying the requirement of pseudooctahedral geometry around nickel(II). On the basis of steric grounds we feel that 3 is a favourable structure and we shall use this in subsequent discussion. In 3, the tridentate ligand spans meridionally. Facial spanning is unlikely since the two nitrogen atoms are separted by only two carbon atoms.[2] We believe that the bridging oxygen in 3 is of the phenolic type.



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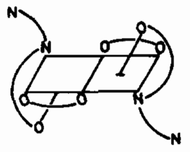
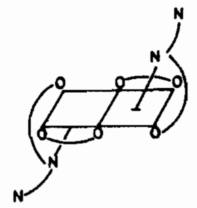


4a



4b

The spectrum of $(hacNEt_2)(hac)Ni$ (Figure 1) has four bands in the range 7000-17,000 cm^{-1}. This spectrum bears distinct similarity to those of square pyramidal Schiff base complexes[2] of nickel(II). In idealised C_{4v} symmetry the four bands can be assigned[7] as: ${}^3B_1\rightarrow{}^3E$, 7400; $\rightarrow{}^3A_2$, 11,000; $\rightarrow{}^3B_2$, 12,900; $\rightarrow{}^3E$, 16,600 cm^{-1}. The feature which most clearly distinguishes this complex from the others described previously is that at 7,400 cm^{-1}. The complex is dimeric in bromoform solution and the same is assumed to be true for the solid state. The square pyramidal geometry around each nickel(II) is satisfied in structures 4a and 4b. We have not been able to choose between 4a and 4b.

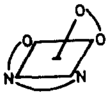
Equilibria in Solution. We shall first discuss the specific case of $(salNEt_2)$ $(sal)Ni$ in chloroform solution. Its electronic spectra in chloroform and bromoform are closely similar. Since the complex is dimeric in freezing bromoform, we believe that the same

(4) P. Pfeiffer and H. Krebs, *J. Prakt. Chem.*, *155*, 77 (1940).
(5) R.H. Balundgi, B. Behera, and A. Chakravorty, unpublished results.
(6) L. Sacconi and U. Campigli, *Inorg. Chem.*, *5*, 606 (1966).
(7) M. Ciampolini, *ibid*, *5*, 35 (1966).

is true of chloroform solution at least upto the freezing point (7°) of bromoform. The ~7500 cm^{-1} band is discernible even at –14° and its intensity increases systematically with increasing temperature; simultaneous intensity changes occur in other regions (Figure 2) resulting in two clearly defined isosbestic points. These spectral changes which are *reversible* with respect to temperature suggest (using Figure 1 as a guideline) that in chloroform solution the equilibrium (1) exists with a measurable population of pentacoordinated species even at –14°.

$$\text{hexacoordinated} \leftrightarrows \text{pentacoordinated} \qquad (1)$$

The equilibrium is not written in the more definitive form $3 \leftrightarrows 4$ since we are not able to exclude the participation of an additional dimeric species in which one nickel(II) is hexacoordinated and the other pentacoordinated. The possible formation of some monomeric five- coordinated species 5 at elevated temperatures can not be excluded. The variable temperature spectral behaviour of the other mixed complexes are qualitatively similar to that of $(salNEt_2)(sal)Ni$. The spectrum (Figure 2) of $(hacNEt_2)(hac)Ni$ at –14° clearly shows that in this case the pentacoordinated species is more abundant. On the other hand in $(salNMe_2)(sal)Ni$ there is no trace of the near-ir band at –14° (Figure 2). Examination of the shapes and intensities of the ~7500 cm^{-1} band has led us to conclude that at a given temperature, the equilibrium concentrations of the pentacoordinated species follow the order: $(hacNEt_2)(hac)Ni > (salNEt_2)(sal)Ni > (salNBu_2)(sal)Ni > (hacNMe_2)(hac)Ni > (salNMe_2)(sal)Ni$. In the case of the last complex the 7500 cm^{-1} band is not clearly observable below 40°.



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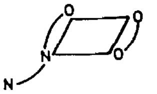

6

Spectra are markedly solvent dependent as can be seen from examination of Figures 2 and 3. In more solvents the terminal ntirogen centre is better stabilised by solvation and the population of the five coordinate species became higher In a number of cases sudied, the equilibrium was found to shift progressively towards the pentacoordinate species in the following order: toluene ~ benzene < chlorobenzene < nitrobenzene < chloroform.

The solution magnetic moment of $(salNEt_2)(sal)Ni$ in toluene remained essentially constant (3.05±0.05 BM, Table IV) over the temperature range (27-71°) of spectral measurements (Figure 3). The possible formation of planar species (which is expected to be diamagnetic) 6 in appreciable amounts is thus excluded at least upto 71°.

We explored the feasibility of the determination of the equilibrium constant for the reaction (1). Unfortunately the spectral bands overlap very considerably and the observed intensity could not be reliably wheighed among the species present. Magnetic data are of no help in this regard since both 3 and 4 are high-spin.

All solution spectral and magnetic data described thus far, were collected at concentrations (~0.02 *M* in nickel(II)) equal to or higher than those used for molecular weight measurements (Table II). In order to see if the monomeric species make any contribution at low concentrations, spectra were recorded at several concentrations for a few compounds. In general the effect of decreasing solute concentration was found to be qualitatively similar to that of increasing temperature. To cite the case of $(salNEt_2)(sal)Ni$ in chloroform at 20°: the intensity of the near-ir band increased by ~5% in going from 0.03 *M* solution to 0.003 *M* solution. There were proportional changes in the expected direction in other regions of the spectrum. The position of equilibrium (1) is not expected to depend on solute concentration. On the other hand the fraction of the monomer in the equilibrium (2) may be expected to increase with decrease

$$\text{dimer} \leftrightarrows 2(\text{monomer}) \qquad (2)$$

in solute concentration. If the monomer has a five-coordinated geometry (e.g. 5) the observed results can be understood. Whether the planar species 6 also makes some contribution at low concentrations (these are too low for magnetic measurements) cannot be decided on the basis of our results.

In pyridine solution, the spectra of the complexes show that the ligand field around nickel(II) has a pseudooctahedral symmetry, with bands at ~10,500 (ε, 12-15), ~13,000 (ε, 3-5), and ~17,000 (ε, 15-20). Variable temperature measurements (–17 to +70°) show only very slight dependence of band intensities on temperature. We conclude that stable pyridine adducts are formed in solution.

Concluding remarks. In Schiff base complexes of nickel(II) varied stereochemistry around the metal ion and solution equilibria amongst various stereoisomers are of common occurrence. The mixed ligand species described in this paper adds one more structural type to this pattern. The behaviour of the present complexes is to be contrasted with that of some monomeric, five-coordinated mixed ligand complexes obtained in solution by mixing bis-bidentate and bis-tridentate Schiff base complexes of nickel(II).[8] Proton magnetic resonance, superexchhange phenomena, synthesis of systems in which the K ligand is replaced by other bidentate species e.g. acetylacetonate anion and three dimensional X-ray crystallography are some of the areas of our further activities in the chemistry of the mixed ligand species.

Experimental Section

Synthesis. This will be illustrated with the specific case of $(hacNMe_2)(hac)Ni$. For other compounds the same general procedure is followed.

(a) In tetrahydrofuran. 2-Hydroxyacetophenone (0.02 mol) was heated to reflux with NN-dimethylethylenediamine (0.02 mole) in 95% ethanol for 2

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(8) I. Bertini and F. Mani, *ibid*, 9, 248 (1970).

hr. Removal of the solvent yielded the crude Schiff base as an orange-red oil. This was then dissolved in dry tetrahydrofuran followed by the addition of potassium *t*-butoxide (0.02 mol) and $(Et_4N)_2$ $NiBr_4$ (0.01 mol). The reaction mixture was stirred for 12 hr in a stoppered flask at room temperature . Removal of tetrahydrofuran on a rotary evaporator followed by repeated extractions (4 x 50 ml) of the green residue with toluene afforded green crystals of the complex. Recrystallization from toluene yielded the pure complex in 30% yield. The same result is obtaied when the Schiff base purified by distillation is used (bp 130-131 at mm; *Anal.* Cald. for $C_{12}H_{18}N_2O$: C, 69.87; H, 8.80; N, 13.58; Found: C, 69.88; H, 8.48; N, 13.42). The other complexes prepared by this procedure were also recrystallised from toluene. However, the complexes $(hprNMe_2)(hpr)Ni$ and $(hbuNMe_2)(hbu)Ni$ are best recrystallised from acetone.

(b) *In Toluene.* To a suspension of $(hac)_2Ni.2H_2O$ (0.01 mol) in 150 ml toluene, NM-dimethylethylenediamine (0.01 mol) was added. The mixture was heated to reflux for 4 hr and during this period it turned dark brown. The filtered solution was concentrated and cooled. The crystals thus obtained were recrystallized from toluene. The yield is 50%.

In the procedure (b) the yield varies in the range 50-80% depending on the compound. For the salicylaldimine complexes the reaction time is considerably less (0.5 hr). The synthetic procedure (b) is much more convenient than the procedure (a). The $(salNMe_2)(sal)Ni$ complexes could also be prepared by using alternative starting materials viz., $(sal)_2Ni.2H_2O$ and $(salNMe_2)_2Ni$ or $(salNMe_2)_2Ni$ and salicylaldehyde as in procedure (b).

Magnetic Measurements were carried out in a Gouy balance described elsewhere.[1] *Electronic Spectra* and *Infrared Spectra* were recorded on Cary 14 recording spectrophotometer having thermostated cell compartments and Perkin Elmer 521 recording spectrometers respectively. *Molecular Weights* were measured cryoscopically in carefully purified benzene and bromoform.

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