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Some Reactions of Bis(N-Haloalkylsalicylaldiminato)-nickel(II) Complexes

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Bis(N-3-Bromopropylsalicylaldiminato)nicke(II) reacts with sodium iodide in acetone to produce the corresponding iodo derivative. Under identical conditions, bis-(N-2-bromoethylsalicylaldiminato)nickel(II) rearranges to form a nickel iodide complex of an imine ether. This is a new example of the template reaction.

Introduction

Some N-2-haloethylsalicylaldimine derivatives of nickel(II) and copper(II), I(X = halogen, n = 2) were prepared by Pfeiffer and Krebs and reported not to undergo the Menshutkin reaction to form ammonium salts with amines.[1] This unreactivity of a halide attached to a chelate side chain is somewhat surprising in view of the known acceleration of such reactions as amidolysis, hydrolysis, ester exchange, racimization, condensation, and proton exchange in the corresponding chelate esters I(X = COOR).[2,3] The reactions of ethers[4] and hydroxyl groups[5] in such systems have also been reported.

The reactivity of the nickel derivatives, I(M = Ni, n = 2, 3, X = halogen) with sodium iodide in acetone has now been investigated. In simple organic systems, the classical Finkelstein reaction is known to involve nucleophilic displacement of the halogen by the iodide.[6] In the present work, the the nature of the reaction products and possibly the course of the reaction is shown to be dependent on the structure of the starting chelate.

Experimental Section

Preparation of N -Haloalkylsalicylaldimines. N-2-bromoethylsalicylaldimine was prepared by the method of Liggett and Diehl,[7] and melted at 55.5-56.5°. This bromide, 5 g, was converted to the corresponding iodide by refluxing for 15 minutes with 10 g of sodium iodide in 50 ml of acetone. The product, recovered by adding water, melted 60-61° after recrystallization from ethanol and was shown to be free of bromide by the sodium iodide in acetone test.

Anal. Calcd. for $C_9H_{10}INO$: C, 39.29; H, 3.66. Found: C, 39.17; H, 3.66.

The infrared spectra of both the above halides are similar with broad OH stretching frequencies at approximately 2700 cm^{-1}, the imine and double bond absorptions in a poorly resolved cluster in the 1630-1580 cm^{-1} region and the out of plane deformation of the benzene ring protons at 745 cm^{-1}.[8] In the 750-400 cm^{-1} region the only significant difference is a band at 545 cm^{-1} found only in the spectrum of the bromide and a band at 502 cm^{-1} found only in the spectrum of the iodide. These are assigned to the carbon halogen stretching frequencies.[8] The proton nuclear magnetic resonance spectra are also similar with a broad singlet at –12.91 ppm (OH), a singlet at –8.35 ppm (N=CH), an aromatic proton multiplet in the 6.67-7.50 ppm range, a triplet at –3.95 ppm (N–CH_2) and a triplet at –3.40 ppm (CH_2I) or at –3.59 ppm (CH_2Br). The ratios of the peak intensities are also in agreement with the structure.

N-3-Bromopropylsalicylaldimine was prepared by adding with rapid stirring to 6 g (0.049 mole) of salicylaldehyde in 25 ml of ethanol, 12 g (0.055 mole) of 3-bromopropylamine hydrobromide in 25 ml of water followed by 2 g (0.05 mole) of sodium hydroxide in 5 ml of water. After stirring for 5 minutes, 40 ml of water were added and the bromo-imine extracted with methylene chloride. Crude 3 bromopropylsalicylaldimine was recovered from this solution after drying over anhydrous magnesium sulfate by removing the solvent at room temperature *in vacuo.* The last traces of methylene chloride were removed by purging with nitrogen.

The above bromide was converted to N-3-iodopropylsalicylaldimine by refluxing for 15 minutes in 200 ml of acetone with 40 g of sodium iodide. The crude iodide was recovered by dilution of the reaction mixture with water, extraction of the iodide with methylene chloride, and concentration of the dried solution at room temperature *in vacuo.* The bromide free product melted at 14-15.°

The infrared spectra of the halopropylsalicylaldimines are similar to these of the ethyl derivatives with the C–Br stretch at 545 cm^{-1} and the C–I stretch

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probably at 490 cm^{-1}, the latter being rather weak. The nmr spectra are also very similar to those of the ethyl derivative with the addition of a quintuplet at −2.17 ppm (CH_2–CH_2–CH_2). The $CH_2N=$ resonace is observed at −3.72 ppm with coupling with the $N=CH$ of $J = 1.3$ cps. The CH_2X triplets are observed at −3.47 ppm (CH_2Br) and −3.25 ppm (CH_2I).

Preparation of Bis(N-Haloalkylsalicylaldiminato)nickel(II) Complexes. Two procedures were used to prepare these complexes. A) Four grams (0.012 mole) of bis(salicylaldehydo) di-aquonickel(II), 0.029 mole of haloalkylamine hydrohalide, and 4 g (0.029 mole) of sodium acetate trihydrate were refluxed in 75 ml of ethanol for 30 minutes.[1] The yield of recrystallized chelate varied from 40-70%. B) Approximately 0.002 mole of the preformed N-haloalkylsalicylaldimine in 15 ml of ethanol with 0.0015 mole of nickel acetate in 10 ml of water were mixed, heated for 3-5 minutes and cooled rapidly. The precipitate, recovered by filtration, was washed successively with water and ethanol, air dried and recrystallized.

Bis(N-3-Chloropropylsalicylaldiminato)nickel(II) was prepared by method A and recrystallized from chloroform and ligroin (bp 60-70°), mp 161-162° dec.

Anal. Calcd. for $C_{20}H_{22}Cl_2N_2NiO_2$: C, 53.14; H, 4.91. Found: C, 53.16; H, 4.83.

Bis(N-3-Bromopropylsalicylaldiminato)nickel(II) was prepared by both method A and B and recrystallized from chloroform and ligroin (bp 60-70°). The green crystals melted 150-152° dec.

Anal. Calcd. for $C_{20}H_{22}Br_2N_2NiO_2$: C, 44.40; H, 4.10. Found: C, 44.67; H, 3.94.

Bis(N-3-iodopropylsalicylaldiminato)nickel(II) was prepared by method B. After recrystallization from carbon tetrachloride the green crystals melted with decomposition over the range 147-155°.

Anal. Calcd. for $C_{20}H_{22}I_2N_2NiO_2$: C, 37.82; H, 3.49; Ni, 9.28. Found: C, 38.16; H, 3.38; Ni, 9.0.

Bis(N-2-Chloroethylsalicylaldiminato)nickel(II) was prepared by method A and melted 178-180° dec. (reported 175-177° [1]) after recrystallization from chloroform.

Anal. Calcd. for $C_{18}H_{18}Cl_2N_2NiO_2$: C, 50.99; H, 4.28; N, 6.61. Found: C, 50.79; H, 4.28; N, 6.42.

Bis(N-2-bromoethylsalicylaldiminato)nickel(II) was prepared by methods A and B and isolated as green needles from hot chloroform. These melted 182-183° dec. with a preliminary transition to an orange-brown material at about 155-160°. Extended heating of this complex in chloroform must be avoiled due to the formation of an insoluble brown precipitate.

Anal. Calcd. for $C_{18}H_{18}Br_2N_2NiO_2$: C, 42.23; H, 3.54; N, 5.47. Found: C, 42.25; H, 3.51; N, 5.50.

Bis(N-2-Iodoethylsalicylaldiminato)nickel(II) was prepared by method B and recrystallized by solution in a minimum amount of boiling methylene chloride, adding an excess of boiling carbon tetrachloride and cooling rapidly. The green plates melted with decomposition at 185-187° with a preliminary transition at about 150-160°.

Anal. Calcd. for $C_{18}H_{18}I_2N_2NiO_2$: C, 35.62; H, 2.99; Ni, 9.67. Found: C, 35.50; H, 2.93; Ni, 9.65.

The infrared spectra of all these complexes are quite similar with all showing the characteristic salicylaldimine absorptions at about 1610 and 1535 cm^{-1}. The out of plane hydrogen deformation frequency characteristic of *ortho* benzene substitution is observed at about 755 cm^{-1} in the propyl derivatives and as a doublet at approximately 735 and 725 cm^{-1} in the ethyl derivatives. The 750-400 cm^{-1} region again is similar for all the propyl halides and also in the case of the ethyl chlorides and bromides and unique frequencies at 640, 540-550, and 495 cm^{-1} can be attributed to the carbon-chlorine, bromine, iodine stretching mode. However the spectrum of the complexed ethyl iodide is quite different from that of the chloride or bromide, in this region, and a unique carbon iodine stretching frequency could not be assigned.

Halogen Exchange of Bromide Complexes with Iodide. Ion. A mixture of 800 mg of bis(N-3-bromopropylsalicylaldiminato)nickel(II), 5.0 g of sodium iodide and 25 ml of acetone was refluxed for 2 hours, stirred overnight at room temperature and again refluxed an additional half hour. The product was isolated by addition of 50 ml of water to the reaction mixture and washing the precipitate consecutively with water and ethanol. The bis(N-3-iodopropylsalicylaldiminato)nickel(II) obtained in low yield was recrystallized from carbon tetrachloride. The infrared spectrum indicated the presence of about 10% of the starting bromide. Shorter or milder reaction conditions increased the amount of bromide in the recovered product. Attempts to remove the bromide by fractional crystallization were not successful.

A mixture of 1 g of bis(N-2-bromoethylsalicylaldiminato)nickel(II), 10 g of sodium iodide, and 50 ml of acetone was stirred at 30° for 3 days. An orange precipitate formed (*vide infra*). Attempts to isolate the iodide from reactions involving shorter reaction times or higher reaction temperatures failed.

The Rearrangement of Bis(N-2-Iodoethylsalicylaldiminato)nickel(II). A suspension of 24 g of bis(N-2-iodoethylsalicylaldiminato)nickel(II) in 500 ml of acetone was refluxed for 48 hours. An orange insoluble precipitate was isolated by filtration and washed with acetone, mp 234-235° dec.

Anal. Calcd. for $C_{18}H_{18}I_2N_2NiO_2$: C, 35.62; H, 2.99; I(ionic), 41.83; Ni, 9.67. Found: C, 35.55; H, 2.82; I(ionic), 41.74; Ni, 9.9.

Analogously prepared from bis(N-2-bromoethylsalicylaldiminato)nickel(II) was the corresponding light buff bromide, mp 182-183° dec. This material slowly hydrolyzed in moist air.

Anal. Calcd. for $C_{18}H_{18}Br_2N_2NiO_2$: C, 42.23; H, 3.54. Found: C, 41.99; H, 3.50.

Rearrangement was also accomplished by heating the bromide or iodide at 140° *in vacuo* for 3-16 hrs. The bromide gave incomplete rearrangement after

3 hrs and observable decomposition over the longer period. Approximately a 1% weight loss was observed over these time periods in 0.1-1.0 g samples. A 168 mg sample of green bromide gave 166 mg of dark brown rearrangement product after heating for 16 hrs at 140° *in vacuo,* mp 174-178°. Heating 145 mg of the green iodoethyl complex at 140° for 5 hrs resulted in the recovery of 142 mg of a red brown complex mp 201-202° dec (mixed mp with rearrangement product produced in acetone solution, 220-222° dec.).

The infrared spectra of the rearrangement products produced by the various techniques are the same. The thermally rearranged (solid phase) products also contain some very weak bands which in keeping with their low melting points are attributed to minor amounts of decomposition products. The ir spectrum of the iodide is almost identical with that of the bromide. Characteristic major peaks in the iodide spectrum are found at 1650 cm^{-1} (imine), 1600 cm^{-1} (benzene), 1200 cm^{-1} (ether) and 750 cm^{-1} (*ortho*. substituted benzene).

Recovery of the Ligand from the Rearrangement Product. The rearranged iodide formed by refluxing bis(N-2-iodoethylsalicylaldiminato)nickel(II) in acetone, 0.98 g, was stirred for 20 min in 15 ml of water to which was added 0.98 g of tetrasodium ethylenediaminetetraacetate tetrahydrate. The white flocculant precipitate which formed was isolated by filtration, washed with water and dried *in vacuo* at room temperature. This precipitate, 0.41 g, (87% recovery) was purified by solution in benzene at room temperature, filtration, concentration of the solution *in vacuo* at room temperature and addition of petroleum ether (bp 30-60°). The recovered buff colored precipitate after drying at 56° *in vacuo,* melted at 73-77° with preliminary softening. The major peaks in the infrared spectrum are found at 1640 and 1600 cm^{-1} (imine), 1250 (ether), and 738-745 (*ortho* substituted benzene) cm^{-1}. No OH or NH stretching frequencies are found. The nmr spectrum shows only a single proton resonance at –8.29 ppm (possibly a triplet, $J = 1.5$ cps, assigned N = CH), a four proton multiplex in the range –6.92 to –7.58 ppm (aromatic protons), and another four proton multiplex in the range –4.00 to –4.42 ppm ($O–CH_2CH_2–N$).

Anal. Calcd. for $C_{81}H_{18}N_2O_2$: C, 73.45; H, 6.16; Mol Wt, 294. Found: C, 73.21; H, 6.57; Mol Wt (osmometric, benzene) 301.

Distillation of 5.2 g of this solid produced 3.0 g of a colorless liquid, bp *ca.* 90° (1 mm). The infrared spectrum of the neat liquid, while differing markedly from that of the precursor in detail, also shows a marked diminution in intensity of the major peak at 1600 cm^{-1}. The nmr spectrum shows a slightly broadened single proton resonance at –8.13 ppm, a four proton aromatic multiplex, and a four proton multiplex at –3.92 to –4.34 ppm (OCH_2CH_2N). The mass spectrum shows three major peaks of approximately equal intensity of mass numbers 147 (molecular ion), 119 (loss of CH_2CH_2) and 91 (loss of CH_2CH_2 and CO).

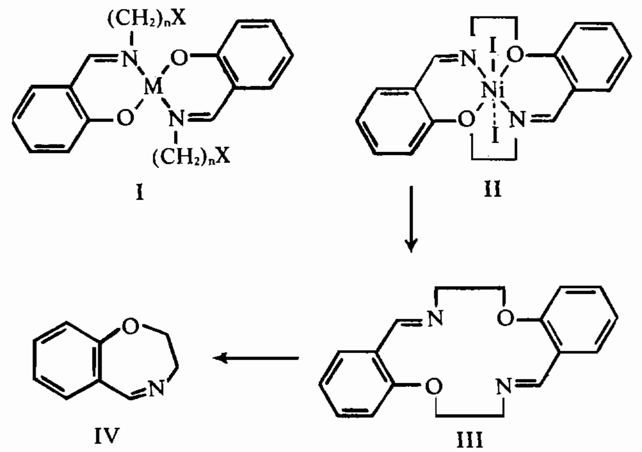
Anal. Calcd. for C_9H_9NO: C, 73,45; H, 6.16; N, 9.51; Mol Wt, 147. Found: C, 73.35; H, 6.28; N, 9.32; Mol Wt (osmometric, benzene) 151.

Upon standing, this monomer, which itself has a melting point below room temperature, solidified. This transformation can be speeded by suspending the liquid monomer in water and adding dry ice. The solid product thus isolated melted partially at 138-142° and completely in the range 170-180°. This material can be sublimed and its physical properties differ most noteably from those of the species described above by the shift of the nmr imine proton resonance to –8.92 ppm and a narrowing of the resonance width. Upon standing this resonance disappears and a broadened peak at –8.21 ppm appears. The mass spectrum of this sublimate is characterized by a low intensity peak at mass number 294 (molecular ion) and the major peak at 266 (loss of CH_2CH_2).

Physical Measurements. Infrared spectra were obtained using samples prepared as mineral oil mulls or neat liquids, mounted on KBr plates, using a Beckman IR 10 spectrometer. Electronic spectra were obtained using a Cary 14 recording spectrophotometer with samples prepared either as mineral oil mulls mounted on filter paper or as chloroform solutions. Nmr spectra were obtained using a Varian A–60 spectrometer on samples dissolved in deuteriochloroform. Shifts were measured from the internal standard tetramethyl silane resonance, with downfield being the negative direction. Magnetic moments were obtained at different fields using an Alpha four inch electromagnet equipped with pole tips tapered to two inches. Mercury(II) tetrathiocyanatocobaltate(II) was used as a calibration standard. Mass spectra were furnished by Mr. J. Lewis of Union Carbide Corporation using a Varian M–66 spectrometer. Molecular weight measurements and elemental analyses were obtained from A. Bernhardt, Mikroanalytisches Laboratorium.

Results and Discussion

The reaction of sodium iodide in acetone with bis(N-3-bromopropylsalicylaldiminato)nickel(II), I (M = Ni, X = Br, n = 3), produces the expected green, square planar iodo derivative, I(X=I). Because of the polyfunctionality of the chelate and the presence of an as yet undetermined slow side reaction which decreases the total yield of I isolated with time, the exchange process does not produce a pure sample of the chelated iodide I. However a comparison of the infrared spectra of the reaction products with those of authentic samples of I(M = Ni, X = Br and also X = I, n = 3) shows that chelates of structure I containing upwards of 90% of the contained halide as the iodide can be obtained in this exchange. Thus the peak at 540 cm^{-1}, assigned as a C–Br stretching frequency, diminishes in intensity with reaction time and the intensity of a peak at 495 cm^{-1}, possibly the C–I stretching frequency, increases with reaction time.



The corresponding reaction of the square planar bis(N-2-bromoethylsalicylaldiminato)nickel(II) with sodium iodide in acetone leads to the isolation of an insoluble orange compound of nominal structure II, having the stoichiometry of, but differing from the expected iodide I(X = I, n = 2). Alternatively II is produced by heating an acetone solution of the iodide I(X = I, n = 2) in the absence of added sodium iodide. A phenomenologically similar but slower transformation is also observed for the pure bromide I(X = Br, n = 2) in the absence of added iodide, but under these conditions the pure chloride is unreactive. The complex II is also formed, in an impure form, by heating the solid green iodide (or bromide)I at 135-150° for several hours.

Unlike I which is diamagnetic, the orange product II is paramagnetic, $\mu_{eff} = 3.12$ B.M. The halogen of II is precipitated instantly by silver nitrate which again contrasts with the much lower reactivity of the halogen in I. Hydrolysis of II with water occurs rapidly at room temperature leading to the isolation of the organic ligand as a nickel free precipitate which contains no hydroxyl groups, is dimeric, and has ir and nmr spectra consistent with the general imine structure, III. The infrared spectrum of the complex II compared with that of the ligand III shows only a small shift of the imine frequencies,[2] but the oxygen-carbon ether stretching frequency is shifted markedly to lower frequencies in the complex. This is in agreement with participation of the oxygen in metal bonding.[9] The electronic spectra of the rearranged products II show a weak d-d transition at 8700 cm^{-1} and a relatively intense charge transfer band at 23,000 cm^{-1} for the iodide.[10] The corresponding bromide has a d-d maximum at 9300 cm^{-1} and a shoulder at approximately 19,000 cm^{-1}. Both complexes have an intense maximum at 31,000 cm^{-1} which corresponds to a maximum at 33,100 cm^{-1} in the free ligand III. Other weak maxima may occur but if present they are obscured by the uneven base line of the mull spectra. Higher frequency d-d transitions in the iodide II are obscured by the charge transfer band. The square planar iodide, I, absorbs at 16,100 cm^{-1} ($\varepsilon = 75\ M^{-1}\ cm^{-1}$), 23,700 ($\varepsilon = 4640$), and 30,000 ($\varepsilon = 9150$). These data are not incompatible with structure II and are somewhat similar to results obtained by Busch and coworkers in reactions of NiN_2S_2 systems with organic halides.[11]

While it is convenient to assign to the rearranged product and the recovered ligand the structures indicated above as II and III, in which the complex has a *trans* arrangement of the iodides and the ligand has a *trans* arrangement around each imine group, alternate structures can not be excluded. Thus the iodo groups can be *cis*, the precipitated complex may be polymeric and the stereo arrangements around the imine bonds might also be *cis-trans* or *cis-cis*. The problem of identification of the structure of II is complicated by the facile interconversion of nickel(II) complexes as well as the interconversion of stereoisomers of imines.[12] Therefore the isolated ligand need not reflect the true stereochemistry of the complexed ligand, nor need the isolated complex II be the initial product of ether formation. As an example of the facile interconversion of the imine compounds, the dimer of nominal structure III is converted to the cyclic monomer IV by distillation. This can be further converted to additional products of identical empirical formula.

Mechanistically, the rearrangement to form II is another example of the " template reaction ", with the course of the reaction being determined by the proximity of the side chain halide and the coordinated phenoxide. The qualitative reaction rates in the absence of added iodide, I > Br > Cl also indicate that bond breaking in the activated complex is important. While the reaction to form II may be an extension of the well known ether synthesis with the chelate furnishing the " phenoxide ion ", the divergent courses of reaction observed here emphasize some of the competitive factors which must be considered in chelate ligand reactivity. In addition to the electrophilic and nucleophilic centers which are involved in the desired reaction, the metal and donor atoms of the chelate also are electrophiles and nucleophiles. In the present system, the electrophilic nature of the nickel atom can be observed by the addition of sodium iodide to an acetone solution of the square planar complex. Using bis(N,n-butylsalicylaldiminato)nickel(II), this results in the formation of a paramagnetic species (method of Evans[13]), containing the salicylaldimine ligand as evidenced by the presence of contact shifts in the nmr spectrum.[2] The iodide ions are probably coordinated to the nickel atom and such anionic species could be important in labilizing the phenoxy group. In the absence of added iodide, the rearrangement of I can be catalyzed by coordination of the alkyl iodide with the nickel atom, a process which would facilitate the cleavage of the carbon halogen bond. Such coordination of alkyl iodides with metal ions is postulated

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in silver(I) catalyzed dehalogenations. However attempts to observe such coordination in the iodide I (X = I, n = 2) by nmr techniques at –65°, conditions under which such cycle formation is favored, were not successful. Such an effect if present is masked by the slowing of the rate of exchange of the predominant square planar diamagnetic species with a paramagnetic isomer.[2]

Finally an analogy can be drawn between the present work and the mechanisms proposed for the reactions of pendent ester groups in bis(N-alkoxycarbonylmethylsalicylaldiminato)metal complexes I(X = COOR, n = 1). Houghton and Pointer[14] have suggested an initial dissociation of a salicylaldimine ligand to form a coordinatively unsaturated species. Intramolecular coordination of the ester group with the metal ion renders the carbonyl carbon electron deficient and facilitates the ester exchange. Alternatively, Verter and Frost[15] have suggested that a phenoxy group involved in chelation assists in the elimination of an ester alkoxide leading to the intermediate formation of a coordinated " phenyl " ester. This reacts rapidly to form the observed products. The present reaction to form II provides an analogy for the Verter and Frost mechanism in which the resulting ether unlike the phenyl ester is unreactive and is therefore isolated.

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