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Monohalo–Tridentate Nickel(II) Complexes. Part II

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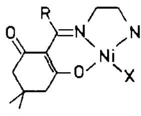
Several monohalo–tridentate nickel(II) complexes were prepared where the halo group is chloro or bromo and the tridentate is a Schiff base adduct of unsymm-N,N-dimethyl and N,N-diethyl-ethylenediamine and one of the following β-dicarbonyl compounds: a derivative of a β-dicarbonyl compound (RCOCHR′COR″; $R = CH_3, R'' = H, R' = C_2H_5OCO$ or CH_3CO; $R = R'' = CH_3$, $R' = C_6H_5$; $R = C_6H_5$, $R' = H$, $R'' = CH_3$ or C_6H_5), a derivative of a 2-acylphenol (o-R-C_6H_4)H; R = H, CH_3, or C_6H_5), 2-hydroxy-1-naphthaldehyde, 1-hydroxy-2-acetonaphthone, or 2-propio-1,3-indanedione. Only the acetylacetone derivatives which contained electron withdrawing groups (C_6H_5, CH_3CO, C_2H_5-OCO) produced the nickel(II) chelates. According to spectral and magnetic data, the normal structure of the complexes is square-planar. Some of the chelates reversibly formed stable hydrates.

Introduction

A question raised by the existence of the halo–tridentate nickel(II) complexes reported in Part I[1] is the structural requirements for the successful isolation of a complex. In Part I, variations in the halogen and the amine portion of the 2-acetyldimedone Schiff base adduct were investigated (dimedone = 5,5-dimethyl-1,3-cyclohexanedione), structure I. The ketone portion is the object of this study. We wish to learn if the tridentates are ubiquitious – practically any combination of the β-diketone and an ethylenediamine will yield the halogen containing nickel complex – or if the β-diketones yielding the chelates are limited.



(I)

$R = H, CH_3, C_2H_5$
$R' = CH_3, C_2H_5$
$R'' = H, CH_3$
$X = Cl, Br, NCS$

Previous workers[1,2] with Schiff base complexes of nickel(II) have generally studied two main groups of ligands: (1) derivatives of β-diketones (such as acetylacetone or ethyl acetoacetate), with derivatives of β-triketones (studied in Part 1) being an interesting subgroup; and (2) derivatives of aromatic hydroxy compounds (such as salicylaldehyde or *o*-hydroxyacetopheone). Following this pattern, we include members of each type in our study.

Experimental

PMR Spectra

These were taken on a Varian HA–100 NMR spectrometer. Tetramethylsilane was used as the internal standard and lock signal. Electronic spectra were taken on a Cary Model 14 spectrometer. For solutions, cells were either 1.00 mm or 1.00 cm in width as required.

Mass Spectra

These were recorded with an AEI MS–9 Mass spectrometer using the direct insertion probe for sample introduction.

Chemicals

All solvents were commercial reagent materials. Chloroform, both normal and deuterated, was passed through a column of neutral aluminum oxide immediately before use. Pyridine was dried over molecular sieves. The nickel(II) bromide · 1,2-dimethoxyethane and nickel(II) chloride · 1,2-dimethoxyethane were obtained from Alfa Inorganics Inc.

Magnetic Susceptibilities

Measurements for solid samples were obtained with a Faraday balance. Mercury(II) tetrathiocyanatocobaltate(II) was the calibrant.[3] Diamagnetic corrections were estimated from Pascal's constants, and the magnetic moments were calculated using the expression, $\mu_{eff} = 2.84\sqrt{\chi_M T}$.[4]

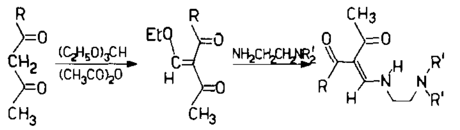
Microanalyses

Analyses were performed by Galbraith laboratories of Knoxville, Tenn.

Synthesis

Ligand synthesis

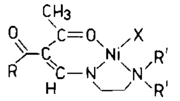
β-diketones were condensed with *unsymm*-N,N-disubstituted ethylenediamines to produce Schiff bases.[5] The β-diketones were all commercial samples except two derivatives of acetylacetone which were prepared by Claisen's procedure.[6]



General synthesis of nickel chelates

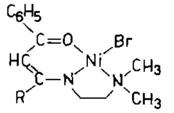
The procedure was similar to that of reference 1. The ligand was combined with a slight excess of sodium ethoxide in ethanol, and then excess nickel(II) halide ·1,2-dimethoxyethane was added. After the mixture had been stirred for about an hour at 60–80° C, the solvent was removed by rotary evaporation. The product was extracted from the remaining solid with hot toluene or with dichloromethane for the less soluble chelates, and recrystallized from toluene–heptane or dichloromethane–heptane.

Chelates obtained



(1) $R = OC_2H_5$, $R' = CH_3$, $X = Br$
(2) $R = OC_2H_5$, $R' = CH_3$, $X = Cl$
(3) $R = CH_3$, $R' = C_2H_5$, $X = Br$
(4) $R = CH_3$, $R' = C_2H_5$, $X = Cl$

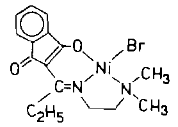
Compounds (1) and (2) were formed in good yield (>50%), are stable, and crystallize well. Because the $R' = CH_3$ of (3) and (4) were insoluble, the $R' = C_2H_5$ analogs were prepared.



(5) $R = CH_3$
(6) $R = C_6H_5$

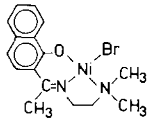
Although complexes, (5) and (6) are readily formed, (5) is less stable as attested by some decomposition on repeated recrystallization of (5).

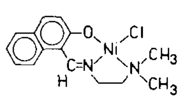
The ligand from 2-proprio-1,3-indanedione yields the corresponding halo–tridentate (7), the 2-methyl analog being too insoluble for study. Compound (7) exists in two forms. One is a brown solid, soluble in dichloromethane; the second is a bright yellow solid, soluble only with difficulty in dichloromethane. The yellow material will yield the brown form on subsequent crystallization, and the yellow form is obtained by evaporating down a solution of the brown.



(7)

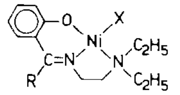
The *unsymm*-N,N-dimethylethylenediamine adducts of 1-hydroxy-2-acetonaphthone and of 2-hydroxy-1-napththaldehyde yielded the monohalo–tridentate nickel(II) complexes, (8) and (9), respectively. The bromo analog of (9) occluded solvent giving inconsistent melting points.





(8)
(9)

Chelates derived from salicylaldehyde (10), acetophenone (11), and benzophenone (12) were also prepared.



(10) $R = H$, $X = Cl$
(11) $R = CH_3$, $X = Cl$
(12) $R = C_6H_5$, $X = Br$

Alternative synthesis

Compound (10) may be prepared by combining the bis(tridentate) complex originally reported by Sacconi *et al.*[7] with a slight excess of nickel(II) chloride·1,2-dimethoxyethane. Upon mixing the two materials in ethanol, the green of the bis(tridentate) nickel chelate is rapidly replaced by the yellow–brown of the halo–tridentate nickel(II) compound. The isolated product has properties identical to those of compound (10) synthesized by the first general method.

The analytical data for the twelve monohalo–tridentate nickel(II) chelates are summarized in Table I.

Hydrates

Compounds (1), (2), and (7) form solid hydrates in a humid atmosphere. On warming the hydrates under reduced pressure, the anhydrous material is recovered, compound (7) requiring an appreciable higher temperature for the conversion compared with (1) and (2). Compounds (3) and (4) also yield hydrates, but they are semisolids and upon dehydration some decomposition is observed. From the weight of water lost, it appears that for (1) and (2) the water to nickel(II) chelate ratio is 2 : 1 whereas for (7) it is 3 : 1.

The five compounds which give hydrates, dissolve in water. All the other chelates do not form hydrates, do not dissolve in water, and do contain aromatic rings. Apparently with the aromatic substituents, the compounds are not sufficiently polar to hydrogen bond with water.

TABLE I. Characterization of some monohalo-tridentate nickel(II) complexes.

Compound	Dec. P.°C[a]	%C		%H		%N		%X	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1	175–176	36.10	36.08	5.23	5.04	7.66	7.61	21.84[b]	21.70
2	209–210	41.12	41.26	5.96	6.10	8.71	8.83	11.03[c]	11.23
3	172–173	39.60	39.64	5.82	5.89	7.70	7.80	21.96[b]	21.80
4	183–184	45.10	45.33	6.62	6.60	8.77	8.62	11.08[c]	11.23
5	181–182	45.45	44.81	5.18	5.14	7.57	7.72	21.60[b]	21.91
6	239–244	52.82	52.61	4.90	4.79	6.48	6.11	18.49[b]	18.34
7	231–232[d]	46.88	46.95	4.67	4.67	6.83	6.97	19.59[b]	19.66
8	275–277	48.77	48.65	4.86	4.78	7.11	7.27	20.28[b]	20.51
9	242–244	53.71	54.04	5.11	4.94	8.35	8.33	10.57[c]	11.04
10	206–207	49.79	49.98	6.11	5.90	8.93	8.74	11.31[c]	11.62
11	247–249	51.33	51.41	6.46	6.39	8.56	8.62	10.82[c]	10.69
12	221–223	52.58	52.70	5.34	4.96	6.45	6.49	18.41[b]	18.05

[a] Uncorrected, complexes melt with decomposition. [b] % bromine. [c] % chlorine. [d] Brown form of 7.

TABLE II.[a] Optical spectra.

Compound	Medium		ν_{Max} cm^{-1}(ε_M)[b]	
1	$CHCl_3$		19,000(264)	
2	$CHCl_3$		19,400(265)	
3	$CHCl_3$		19,300(262)	
4	$CHCl_3$		19,300(294)	
5	$CHCl_3$		19,200(217)	15,900(63)
6	$CHCl_3$		19,300(293)	16,000(80)
7	CH_2Cl_2		18,500(208)	15,400(51)
7-brown	Nujol	22,200(1.00)[c];	16,900(0.76)	11,800(0.26)
7-yellow	Nujol	23,500(1.00)[c];	16,100(0.28)	11,400(0.17)
8	$CHCl_3$		19,600(321)[d]	15,700(105)
9	$CHCl_3$		19,700(380)[d]	16,400(80)[d]
10	$CHCl_3$		19,300(294)	
11	CH_2Cl_2		19,200(244)	16,100(70)[d]
11	Nujol	18,900(1.00)[c];	13,400(0.83)	9,740(0.54); 5,090(0.30)
12	$CHCl_3$		19,200(280)	15,900(70)[d]

[a] All data obtained at room temperature. [b] Molar extinction coefficients (cm^{-1}M^{-1}). [c] Relative intensities cited for Nujol mulls. [d] Shoulder to band at higher ν_{max}.

Results

In chloroform solution, all the monohalo–tridentate nickel(II) chelates reported here are square–planar as indicated by the absence of any absorption below 15,000 cm^{-1} in the optical spectra (Table II). Furthermore, the pmr spectra of the complexes in deuterated chloroform show no contact shifts, except in the case of (7). The hydrates attain a square-planar configuration in chloroform, the water molecules being dissociated from the nickel(II) in solution.

In the solid state, the square-planar form is also displayed by the monohalo–tridentate nickel(II) chelates except for the hydrates, and compounds (7) and (11). Only these exceptions are paramagnetic (Table III), the rest having moments less than 0.6 B.M., and only these exceptions show absorptions below 15,000 cm^{-1} in the optical spectra of the Nujol mulls (Table II).

Compound (7) presumably has a pseudo-octahedral structure due to intermolecular association. The association seems to be weaker in the brown form than in the yellow. The former has a lower magnetic moment than the latter, and the intensity ratio of the 11,000 cm^{-1}

TABLE III. Magnetic moments of solid samples.

Compound	μ_{eff}(B.M.)	Compound	μ_{eff} (B.M.)
1 dihydrate	3.10	7 yellow	3.10
2 dihydrate	3.03	7 brown	1.67
		7 trihydrate	3.10
		11	3.18

TABLE IV. Proton chemical shift data.[a]

Cpd. 3	CH_3 ethyl	CH_2N	CH_3 Keto	CH_3CO	CH_2 ethyl	CH_2 ethyl	NCH_2	CH
	1.92(t)[b]	2.24(t)	2.29(s)		2.64(m)	3.36(m)	3.41(t)	7.60(s)
Cpd. 4	CH_3 ethyl	CH_2N	CH_3 Keto	CH_3CO	CH_2 ethyl	CH_2 ethyl	NCH_2	CH
	1.93(t)	2.23(t)	2.30(s)		2.55(m)	3.24(m)	3.41(t)	7.50(s)
Cpd. 7	CH_3 ethyl	CH_2 ethyl	CH_2N	$(CH_3)_2N$	NCH_2	C_6H_4		
dilute	1.32(t)	3.15(q)	3.76(b)	5.16(s)	5.60(b)	7.2–7.9		
conc.	1.66(t)	3.24(q)	6.30(b)	9.45(s)	9.70(b)	7.0–8.0		

[a] Chemical shifts of solutions measured in ppm from an internal standard, tetramethylsilane; the solvent is $CDCl_3$.
[b] Abbreviations: b = broad; m = multiplet; q = quartet; s = singlet; t = triplet.

band to the 16,000 cm^{-1} band in their optical spectra, is smaller for the former than for the latter. This evidence for greater association in the yellow form is in keeping with the lower solubility of the yellow species as compared with the brown and with the fact that the yellow is produced on evaporating off the solvent whereas the brown crystallizes from solution. Of all the compounds studied here, only compound (7) was sufficiently soluble and associated in solution to show a marked change of chemical shift with concentration (Table IV), the $(CH_3)_2N$ resonance shifting upfield more than 4 ppm upon dilution. Concentration-dependent chemical shifts for monohalo–tridentate nickel(II) complexes were reported in Part I.[1] Apparently the β-diketone moiety of the indane ring in compound (7) is conducive to association as is the β-diketone group of the dimedones studied in Part I.

The structure of compound (11) in the solid state is not obvious. The low frequencies of the three absorptions in the spectrum of the Nujol mull are more indicative of a tetrahedral than an octahedral geometry. According to tetrahedral symmetry, the bands may be assigned $^3T_1(F) \rightarrow {}^3T_2(F)$, 5,090 cm^{-1} and 9,740 cm^{-1}; $^3T_1(F) \rightarrow {}^3A_2(F)$, 13,400 cm^{-1}; $^3T_1(F) \rightarrow {}^3T_1(P)$, 18,900 cm^{-1}. For tetrahedral nickel(II) compounds of low symmetry, the $^3T_1(F) \rightarrow {}^3T_2(F)$ transition is often split but the bands generally occur below 9,000 cm^{-1}. Also the $^3T_1(F) \rightarrow {}^3A_2(F)$ transition usually lies between 10,000 and 12,000 cm^{-1}.[8] On the other hand, the low solubility, high melting point, and magnetic moment of 3.18 B.M. are suggestive of an octahedral configuration. The magnetic moment of tetrahedral nickel(II) complexes usually exceed 3.2 B.M.[9] Why the acetophenone compound (11) is more associated than the corresponding salicylaldehyde compound (10) or why compound (11) is distorted towards a tetrahedron while the naphthalene (8) is not remains an unsolved question.

For the three hydrates of (1), (2) and (7), the magnetic moments and spectra of the Nujol mulls support a pseudo-octahedral configuration. The spectra are similar to those reported for powdered samples of the six-coordinate, dihydrates of bis(salicylaldehydato)- and bis(acetylacetonato)nickel(II), although at somewhat higher frequencies than noted for the latter two hydrates.[10] In the trihydrate of compound (7), one of the water molecules is presumably hydrogen bonded to a ligand site.

With regard to the optical spectra (Table II) the introduction of phenyl groups has two effects. First the degeneracy of the ligand field transitions is reduced in that besides an absorption near 19,000 cm^{-1}, a second, less intense band is found at about 16,000 cm^{-1} for all compounds containing a phenyl group, except compound (10). Second, the intensities of the absorptions are increased, compare (5) with (6), (11) with (12), and the naphthalene derivatives (8) and (9) with the benzene analogs (11) and (12).

In the pmr spectra (Table IV), all the chelates containing the $-NCH_2CH_2N(C_2H_5)_2$ moiety exhibit four methylene resonances. For some compounds, the two low field bands overlapped, but addition of about 10% by volume of deuterio-benzene to the deuterio-chloroform solutions separated the two resonances. In the spectra with sufficient resolution to clearly detect the multiplet structure of the bands, the two intermediary methylene resonances appear as 1:3:4:4:3:1 hextets and the lowest and highest methylene resonances appear as 1:2:1 triplets. The triplets are attributed to the bridging methylene groups of the ethylenediamine moiety. The hextet structure indicates that the protons of a methylene group in each ethyl substituent are not equivalent but rather exhibit a gem coupling of about 14 Hz and a vicinal coupling to the neighboring methyl group of about 7 Hz, with a chemical shift difference between the hextets of more than 0.7 ppm. Similar nonequivalence of methylene protons has been noted for other ethyl derivatives such as diethyl sulfite.[11] In the monohalo–tridentate nickel(II) complexes, the nonequivalent environment of the methylene protons may rise from the puckered structure of the ethylenediamine ring. This nonequivalence was also reported in Part I.

Conclusion

The nickel(II) complexes prepared here, as in Part I, are unusual in that they contain nickel(II) bonded to one halo ligand and one uninegative tridentate ligand. Several nickel(II) compounds are known in which the tridentate ligand is neutral giving rise to the five-coordinate $NiLX_2$ species[12–15] and in a few cases the four-coordinate ionic [NiLX]X.[16] If the tridentate ligand has a –l charge, the isolated nickel(II) complexes usually contain two tridentate ligands per nickel ion, NiL_2.[7, 17–19] When sulfur is one of the coordinating atoms in a uninegative tridentate ligand, dimerization, $(NiL)_2$, with the sulfur acting to bridge the two nickel atoms is possible.[20]

Sacconi and Speroni did prepare a monoiodo–tridentate nickel(II) complex by combining the adduct of *o*-methylthiobenzaldehyde and N,N-diethylethylenediamine with nickel(II) iodide and demethylizing the sulfur atom of the Schiff base in the reaction.[21] In their studies of tridentate ligands formed from salicylaldehyde and N,N-disubstituted ethylenediamine, however, Sacconi and his collaborators reported isolating only the bis(tridentate)nickel(II) complexes.[7] They did prepare monohalo–tridentate complexes of copper(II).[22] These copper(II) chelates were synthesized by either reacting a copper(II) halide with the tridentate Schiff base ligand in alcohol or by refluxing the bis(tridentate) copper(II) compounds in a chlorine-containing solvent such as chloroform and carbon tetrachloride. We find that the bis(tridentate) nickel(II) compounds do not undergo such a dehalogenation of solvents but that some will react with nickel(II) halide to form the monohalo–tridentate nickel(II) compounds, such as compound (10). In the future we will investigate the applicability of this synthetic procedure.

Apparently Schiff bases of aromatic hydroxy compounds (both aldehydic and ketonic) yield monohalo–tridentate nickel(II) chelates (9)–(12). However the situation with the other important group of Schiff Base ligands – the *β*-diketones – is far more complex.

We could not prepare chelates from the two of the more commonly used *β*-diketones – acetylacetone or ethyl acetoacetate. The failure of the latter is likely due to the poor coordinating ability of the acetotacetate group.

The ketones, 3-phenylacetylacetone and 3-phenylthioacetylacetone, did give monohalo–tridentate nickel(II) complexes as evidenced by mass spectra and the characteristic purple color, but the materials decomposed upon crystallization.

The marginal stability offered by these two 3-substituents may be attributed to the electron withdrawing effect of the two moieties. Presumably the electron withdrawing of the 3-phenyl group is *via* induction rather than conjugation, for in bis(3-phenyl-2,4-pentanedionato) copper(II), the phenyl group is twisted through a torsional angle of 70° from the mean plane of the chelate ring which, according to Carmichael *et al.*, reduces the resonance interaction by about 34%.[23]

It can be concluded from our study, that the two methyl groups of acetylacetone destabilize the mono-' halo–tridentate nickel(II) chelates. Substitution of one methyl moiety by a phenyl group does yield such a chelate (5), and with both methyl substituents replaced by phenyl groups, complex (6) is obtained, which is more stable than (5). Similarly, substituting a hydrogen for a methyl group leads to stability, for although 3-carbethoxy- and 3-acetyl-acetylacetone did not yield monohalo–tridentate nickel(II) chelates, the analogous acetylacetaldehyde compounds did. Presumably the destabilizing effect of the methyl substituents is a result of the electron donating property of these groups. It is interesting that the influence of a methyl group is also noted in the aromatic systems, with compound (11) having magnetic and spectral properties differing from those of (10) and (12).

In addition to providing the first neutral monohalo–tridentate nickel(II) chelates, these compounds are of interest because the halogen can be exchanged by a variety of moities. In part I of this series, the replacement of the halogen by the pseudo halogen SNC^- was mentioned. We are currently investigating the more interesting cases of exchanging the halogen by anions of *β*-diketones to generate 5-coordinated nickel(II) complexes and of the dephenylation of boron occurring when the anion is tetraphenylborate.

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