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INTERACTION OF AMINES AND SOME NICKEL (II)-SCHIFF BASE COMPOUNDS—II

ADDUCT FORMATION(1)*

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Abstract—The interaction of amines with carbonyl compounds of nickel (II) is discussed, and the isolation of several new compounds is reported. The ability of some nickel (II) salicylaldimes and β-ketoimines in solution to expand from planar to octahedral coordination with addition of bases such as pyridine is examined spectrophotometrically. The isolation of several pyridine adducts is reported.

Two kinds of interactions between an amine and a nickel (II) chelate compound may be expected. First, the amine may co-ordinate to the nickel (II) ion, forming a new compound in which nickel has an expanded coordination number. Secondly, reaction with the coordinated ligand may occur, such as condensation with a β-diketone to form a β-ketoimine, or in the case of imine coordination, $>C=N\rightarrow Ni(II)$, the interaction may result in amine exchange or transamination.(1) The first type of interaction has been observed for a number of planar nickel chelate compounds,(2) including the interaction of bis(2,4-pentanediono)nickel (II) and pyridine in solution,(3) and by isolation of the bispyridine compound,(4–6) in addition to the diammine and bisaniline adducts.(7) The bis(ethoxyacetylacetono)bis(pyridine)nickel (II) compound has also been isolated.(8) There is also evidence for adduct formation occurring with nickel (II)-Schiff base compounds. Evidence for interaction between bisacetylacetone-ethylenediimino-nickel (II) and ethylenediamine(9) and between bis(N-methylsalicylaldimino)-nickel (II) and 1:10-phenanthroline(10) consisted of isolation of the solid "adducts." Bis(N-*m*-tolysalicylaldimino)bis(pyridine)nickel (II) and other adducts were obtained by adding light petroleum to the saturated pyridine solutions of the parent compound.(11) Also, isolation of the diammine bisacetylacetoneethylenediimino-nickel (II) has been reported. On the other hand, PFEIFFER and co-workers found

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(1) For part I in this series, see *J. Inorg. Nucl. Chem.* **27**, 345 (1965).

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that pyridine could be used as a recrystallizing solvent for bis(*o*-hydroxyacetophenoneimino)nickel (II),(12) bis(salicylaldimino)nickel (II), and other nickel (II)-salicylaldimines,(13) although bissalicylaldehyde-*o*-phenylenediiminonickel (II) absorbed two moles of pyridine which could easily be removed *in vacuo*.(14) Basolo and Matoush(15) also isolated the latter adduct, in addition to the bispyridine compounds of bis(N-phenyl- and N-methylsalicylaldimino)nickel (II).

EXPERIMENTAL

Preparation of nickel (II)*-chelate compounds*

The preparations of the nickel (II)-salicylaldimine compounds were reported earlier.(1) The synthesis and properties of the nickel (II)-*β*-ketoimines are reported elsewhere.(16–20)

Bis(2,4-*pentanediono*)*nickel* (II) *dihydrate*. A solution of 24·88 g (0·1 mole) of nickel (II) acetate tetrahydrate in 50 ml of water was added slowly, with stirring, to a solution of 22·0 g (0·22 mole) of acetylacetone in 100 ml of ethanol. The solution became dark green in colour. Aqueous sodium hydroxide (ca. 5 M) was added slowly until formation of a blue precipitate was no longer observed. The precipitate was filtered off, washed with 100 ml of water, and allowed to dry in the atmosphere. M.p., 240°C. Yield, 88%. (Found: C, 41·31, H, 6·55; Calc. for $NiC_{10}H_{14}O_4 \cdot 2H_2O$; C, 41·00, H, 6·15%).*

Bis(1,1,1-*trifluoro*-2,4-*pentanediono*)*nickel* (II) *trihydrate*. Nickel (II) acetate tetrahydrate (14·4 g or 0·05 mole) was dissolved in 150 ml of warm water, and a solution of 15·4 g (0·1 mole) of trifluoroacetylacetone in 25 ml of ethanol was added. The mixture was warmed and stirred, and after addition of 1·2 g of anhydrous sodium carbonate, it was heated for 15 min. The blue precipitate which formed was filtered off and recrystallized from 50 per cent aqueous ethanol. M.p. 283°(d)C. Yield 68%. (Found: C, 28·66, H, 3·34; Calc. for $NiC_{10}H_8F_6O_4 \cdot 3H_2O$, C, 28·71, H, 3·52%).

Bis(1,1,1,5,5,5-*hexafluoro*-2,4-*pentanediono*)*nickel* (II) *trihydrate*. This compound was prepared by the method used for the preceding compound. M.p., 219–221°C. Yield, 46%. (Found: C, 22·82, H, 1·70; Calc. for $NiC_{10}H_2F_{12}O_4 \cdot 3H_2O$, C, 22·78, H, 1·52%).

Adduct formation

The general procedure used for the formation of adducts between nickel carbonyl compounds and amines is exemplified by the following preparation;

Bis(2,4-*pentanediono*)*di*(*butylamine*)*nickel* (II). To a solution of bis(2,4-pentanediono)nickel (II) (1·25 g or 0·005 mole) in 300 ml of warm benzene was added 1·5 g (0·02 mole) of butylamine in 50 ml of benzene. The solution was refluxed for two hr, cooled, and evaporated to 100 ml. Upon cooling, a light blue, fibrous precipitate formed which was filtered and washed with cold benzene (Cf. Table 1).

Spectra and continuous variation studies

The spectra of nickel (II)-chelate compounds were observed over the range 360–660 m*μ* by means of a Beckman Model DU spectrophotometer. The spectra were examined for adherence to Beer's Law. The interaction of nickel (II)-chelate compounds with pyridine in chloroform and xylene solutions was studied using the method of continuous variations (salicylaldimines at 540–560 m*μ*, *β*-ketoimines at 380–420 m*μ*).

* All microanalyses were performed at the University of Illinois under the direction of Mr. J. Nemeth.

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DISCUSSION

There is ample evidence for the interaction of bis(β-diketono)-nickel (II) compounds with bases allowing for expansion of the coordination number from four to six. This information is significant for two reasons. First, it indicates the possibility that condensation of amines with the carbonyl ligand may involve preliminary co-ordination of the amine with nickel. Secondly, it indicates several important characteristics concerning the nature of the nickel (II)-β-diketones.

TABLE 1.—REACTIONS OF AMINES WITH CO-ORDINATED CARBONYL COMPOUNDS

Metal compound[a]	Base	Solvent	M.p.(°C)	Analysis[b]		
				C	H	N
A	Pyridine[c]	Benzene	188–190	59·29	5·93	6·92
				59·54	5·73	6·61
A	Butylamine	Benzene	193–195	53·64	8·95	6·95
				53·59	8·93	7·03
A	Benzylamine	Benzene	234–235	61·19	6·80	5·95
				60·06	6·81	5·56
B	Butylamine	Ethanol	139	64·29	6·82	6·82[d]
				64·02	6·87	7·01
B	Benzylamine	Ethanol	207	70·20	5·02	5·85[d]
				70·64	5·27	6·06
C	Butylamine	Ethanol	158–160	60·67	7·58	5·90
				60·07	7·71	5·61
C	Benzylamine	Ethanol	207–210	71·04	5·53	5·53[d]
				69·95	5·73	6·08
D	Pyridine	Benzene	200–202	45·91	3·21	5·36
				45·67	3·64	5·31
D	Butylamine	Benzene	169–172	42·30	5·87	5·48
				41·70	6·06	5·04
D	Benzylamine	Benzene	190–191	49·77	4·49	4·84
				49·39	4·78	4·79
E	Pyridine	Benzene	110	37·68	1·88	4·40
				38·03	2·17	4·45
E	Butylamine	Benzene	142–144	34·92	3·88	4·53
				34·36	4·29	4·38
E	Benzylamine	Benzene	159–161	41·95	2·91	4·08
				42·46	3·15	4·18

[a] A, bis(2,4-pentanediono)nickel (II); B, bis(salicylaldehydo)nickel (II); C, bis(*o*-hydroxyacetophenono)nickel (II); D, bis(1,1,1-trifluoro-2,4-pentanediono)nickel (II); E, bis(1,1,1,5,5,5-hexafluoro-2,4-pentanediono)nickel (II).

[b] First line, calculated; second line, found.

[c] All products were formed as adducts, NiCh$_2$·2B, unless otherwise indicated.

[d] Condensation product formed.

Previous work[1] has indicated that, although the nickel (II) derivatives of salicylaldehyde and β-diketones are formally similar, they are markedly different in their interaction with amines. The addition of an amine to bis(salicylaldehydo)nickel (II) always resulted in the isolation of the N-substituted bis(salicylaldimino)nickel (II) (cf. Table 1). However, when amines were added to bis(2,4-pentanediono)nickel (II) no condensation was evidenced. Instead, only diamine adducts were obtained, using butylamine or benzylamine, or unreacted starting material was recovered, using aniline. Addition of an excess of calcium sulphate to the solution did not lead to condensation, nor did the addition of small amounts of acetic acid serve to catalyse Schiff base formation.

Several differences may be noted between the salicylaldehyde and β-diketone ring systems. Both from six-membered chelate rings, but the acetylacetone ring derives added stability from resonance interactions. The insertion of the benzene ring into the chelate-ring system of salicylaldehyde would tend to give slightly different bond angles to groups on the carbonyl carbon atom which could have steric consequences. For example, the carbonyl carbon atoms of *o*-hydroxyacetophenone and of acetylacetone both contain methyl groups which would offer greater steric hindrance to an incoming amine than the proton of the carbonyl carbon in salicylaldehyde. Molecular models show that the steric effects of the methyl groups of *o*-hydroxyacetophenone and acetylacetone are essentially the same with respect to N-substituted derivatives of their Schiff bases. The positive inductive effect (cf. GOULD(21)) of the methyl group on the carbonyl carbon atom is perhaps a more significant factor in reducing nucleophilic attack by an amine base. It has been suggested(22) that the mechanism for the condensation of an amine with bis(salicylaldehydo)nickel (II) involves a nucleophilic attack by the amine on the carbonyl carbon atom. The latter, due to the polarization effects of the nickel ion, would become a centre of positive charge.

Since the metal ion-β-diketone system is stabilized to a greater extent by resonance interaction than the analogous salicylaldehyde species, there would by a greater disruption of bonding in the β-diketone system than the salicylaldehyde system when attack by an amine takes place. Also, in the β-diketone-metal compound, each carbonyl carbon is affected equally by the inductive and polarization effects of the nickel (II) ion, while in the salicylaldehyde compound the chelate ring system is more heterogeneous, and there is but one carbonyl carbon atom which can be influenced by the metal ion. Finally, the positive inductive effect of the terminal methyl groups upon the carbonyl carbon atoms in acetylacetone (and *o*-hydroxyacetophenone) would tend to make them less susceptible to nucleophilic attack by an amine base.

The failure of amines to condense with acetylacetone could be a result of the positive inductive effect of the methyl group. However, when trifluoroacetylacetone and hexafluoroacetylacetone were used instead, only the bis(β-diketono)-diaminenickel (II) adducts were obtained. The negative inductive effect of the fluoro atoms would reduce the electron density of the carbonyl carbon atom presenting a more favourable situation for nucleophilic attack. Since condensation did not occur, it is apparent that resonance stabilization is a more significant factor in preventing condensation involving coordinated β-diketones than are inductive effects.

Condensation was observed in all cases when amines were added to bis(salicylaldehydo)nickel (II). With bis(*o*-hydroxyacetophenono)nickel (II) condensation was observed with benzylamine, but not with the weaker base, butylamine. Hence, the presence of the methyl group on the carbonyl carbon atom has a limited but meaningful influence upon the nature of the carbonyl grouping.

Several experiments were performed in an attempt to isolate pyridine adducts of nickel (II)-β-ketoimines. Bis(4-iminopentane-2-ono)nickel (II) was refluxed in

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pyridine, but it was not possible to isolate the pyridine adduct. In fact, the solvent was found to be ideal for recrystallization of the β-ketoimine-nickel salt. There was no indication of adduct formation (in a methanolic solvent) between bis(4-iminopentane-2-ono)nickel (II) and 1 : 10-phenanthroline, as evidenced by recovery of the unreacted starting materials. However, bis(3-phenylimino-1,3-diphenylpropane-1-ono)nickel (II) when recrystallized from pyridine seemed to contain some pyridine of crystallization which could be removed by recrystallization from benzene.

TABLE 2.—ADDUCT FORMATION OF NICKEL(II)–SCHIFF BASE COMPOUNDS WITH PYRIDINE

	Δ VALUES[a]									
	Mole Fraction Nickel (II)									
	1·0	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·2	0·1
Compound[b]										
I	0·000	0·006	0·009	0·016	0·016	0·019	0·024	0·020	0·013	0·006
II	0·000	0·015	0·019	0·025	0·034	0·039	0·046	0·055	0·033	0·015
III	0·000	0·009	0·020	0·024	0·026	0·028	0·033	0·042	0·025	0·020
IV	0·000	0·006	0·004	0·001	0·002	0·007	0·001	−0·005	0·006	−0·001
V	0·000	0·018	0·007	0·006	0·015	0·015	0·011	0·003	0·004	0·003
VI	0·000	0·002	−0·002	−0·003	0·002	0·005	−0·002	0·000	0·001	0·001
VII	0·000	0·003	0·007	0·007	0·012	0·002	0·003	0·005	0·007	0·005
VIII	0·000	0·010	0·009	0·005	0·000	0·002	0·000	0·010	0·010	0·014
IX	0·000	0·020	0·034	0·047	0·062	0·067	0·070	0·062	0·045	0·012
X[c]	0·000	0·001	0·002	0·003	0·002	0·002	0·001	0·002	0·001	0·002
XI	0·000	0·002	0·020	0·028	0·030	0·022	0·018	0·015	0·006	0·001

Compound[b] ——	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Wavelength (mμ)	550	380	420	406	560	625	540	550	455	640	540
Conc. × 10^3 M[d] nickel (II) ion	20	0·1	0·064	0·1	7·5	7·5	3·7	3·7	1·0	6·8	10
Conc. × 10^3 M pyridine	20	0·1	0·072	0·1	7·5	7·5	4·2	4·2	0·97	6·2	9·3

[a] $\Delta = D_{calc} - D_{obs}$

[b] I, bis(4-iminopentane-2-ono)nickel (II); II, bis(3-phenylimino-1-phenylbutane-1-ono)nickel (II); III, bis(3-phenylimino-1,3-diphenylpropane-1-ono)nickel (II); IV, bis [4-(2,6-dimethyl)phenyliminopentane-2-ono]nickel (II); V, bisacetylacetoneethylenediiminonickel (II); VI, bisbenzoylacetoneethylenediiminonickel (II); VII, bissalicylaldehydeethylenediiminonickel (II); VIII, bis(4-methylsalicylaldehydeethylenediimino)nickel (II); IX, bis(salicylaldimino)nickel (II); X, bis-(*N*-ethylsalicylaldimino)nickel (II); XI, bis(N-n-butylsalicylaldimino)-nickel (II).

[c] Xylene used as solvent, all others in chloroform.

[d] Two compounds, bis(N-phenylsalicylaldimino)nickel (II) and bis(*o*-hydroxyacetophenoneimino)nickel (II), were but slightly soluble in most common solvents. Bis(N-methylsalicylaldimino) nickel (II) did not follow Beer's Law.

Several salicylaldimine and β-ketoimine compounds of nickel (II) were studied by means of Job's titrations with pyridine in chloroform or xylene (Table 2). Pyridine was chosen to avoid amine exchange side reactions. Poor solubility in chloroform, benzene, methanol and xylene, e.g., bis(*o*-hydroxyacetophenoneiminonickel (II) and bis(N-phenylsalicylaldimino)nickel (II), or large divergence from Beer's Law, e.g., bis-(N-methylsalicylaldimino)nickel (II), were factors limiting the number of compounds which could be examined.

Of the salicylaldimines investigated, those containing quadridentate ligands gave little or no evidence of coordinating with pyridine [bis-salicylaldehydeethylenediiminonickel (II) and bis(4-methylsalicylaldehydeethylenediimino)nickel (II)] while nickel salts with bidentate ligands were found to coordinate with two moles of pyridine (bis(N-n-butylsalicylaldimino)nickel (II) and bis(salicylaldimino)nickel (II)).

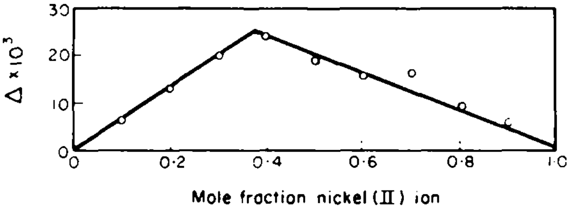

FIG. 1.—Job's titration; bis(4-iminopentane-2-ono)nickel (II) (0·02 M) *versus* pyridine (0·02 M) in chloroform solvent at 550 mμ.

Among the nickel-β-ketoimine compounds, bis(4-iminopentane-2-ono)nickel (II), bis(3-phenylimino-1-phenylbutane-1-ono)nickel (II), and bis(3-phenylimino-1,3-diphenylpropane-1-ono)nickel (II) were found to coordinate with pyridine (two moles), but bis[4-(2,6-dimethyl)phenyliminopentane-2-ono]nickel (II) did not co-ordinate inasmuch as the phenyl ring of the latter compound lies perpendicular to the plane of the chelate ring, as indicated by molecular models, the methyl groups would point along the *z*-axis, and it seems probable that the steric hindrance which would arise as a result could inhibit pyridine from coordinating to the nickel (II) ion.

While solid adducts of β-diketone-nickel compounds are easy to isolate, this is not always true of the β-ketoimine- and salicylaldimine-nickel compounds. However, many of the latter two types do give indication of adduct formation in solution and do provide further examples of the ease of expansion of coordination number.

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