

cates that association as shown by eq 3 is not occurring. Furthermore, the absence of temperature-dependent shifts of the ligand proton resonances in inert solvents argues against the formation of associated species in coordinating solvents.

It would be expected that solvating power, steric effects, and solvent $10Dq$ might be contributing factors to the ΔH° values. However, except for NiCR^{2+} in water and DMF the ΔH° and ΔS° values are quite similar, being about $4.4 \pm 0.4 \text{ kcal mol}^{-1}$ and $12 \pm 3 \text{ cal mol}^{-1} \text{ deg}^{-1}$, respectively. Therefore it seems probable that a number of compensating factors may be at work and a qualitative analysis of the ΔH° values would be futile.

The ΔH° value for NiCR^{2+} in water is the most negative, consistent with the recent proposal by Busch³ that solvent structure breaking is an important factor. However NiCRCH_3^{2+} in water has a rather normal ΔH° and it seems unlikely that introduction of a methyl

group on the Schiff base would have a significant effect on the solvent structure.

The hyperfine coupling constants (A/\hbar) in Table IV have all been calculated with the assumption that $\mu_\infty = \bar{g}\sqrt{S(S+1)} = 3.00 \text{ BM}$. It would seem likely that this assumption is good to within at least $\pm 5\%$ and therefore the variations in A/\hbar for different systems are real. The nature of the axial ligand, solvation of the octahedral complex, and minor changes in geometry of the macrocyclic ligand are likely to affect A/\hbar . Therefore the observed variations are not considered to be unusual.

Finally it should be noted that the equilibrium constant parameters were determined for use in a study of the bulk solvent nmr in these systems. The values reported here have served adequately to correct both the solvent proton chemical shifts and line broadenings. The results of the latter study will be reported in a subsequent paper.¹

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Monohalo Tridentate Nickel(II) Complexes

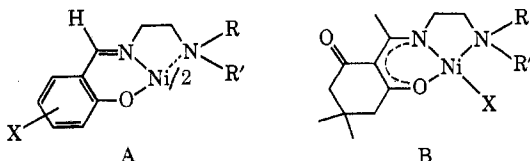
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Received January 19, 1971

Neutral monohalo tridentate nickel(II) complexes have been synthesized and their magnetic and spectral properties described in which the halo (or pseudohalo) group is Cl, Br, or NCS and the tridentate ligand is an *N*- β -R,R'-aminoethyl-2-acetiminodimedonate or -2-formyldimedonate anion with R = R' = alkyl or R = H, R' = alkyl. According to the magnetic moment values, the ligand field, and pmr spectra, intermolecular interaction occurs for some of the complexes in the solid state and in chloroform solution, the amount of association decreasing in the order Br > Cl > NCS; formyl > acetyl; and, for the *N*- β -R,R' substituent, $\text{N}(\text{CH}_3)_2 > \text{N}(\text{H})\text{CH}_3 \geq \text{N}(\text{H})\text{C}_2\text{H}_5 > \text{N}(\text{C}_2\text{H}_5)_2$. The R = H derivatives form 1:1 adducts with chloroform which have properties characteristic of high-spin, five-coordinate nickel(II) complexes. As this is the first report of neutral monohalo tridentate nickel(II) compounds, factors conducive to the formation of such nickel(II) complexes are considered.

Introduction

Numerous bis(*N*- β -R,R'-aminoethyl-X-salicylaldiminato)nickel(II) compounds, abbreviated $\text{Ni}[\text{X-Sal-en-N}(\text{R})\text{R}']_2$, structure A, have been investigated by Sacconi, *et al.*^{1,2} We have found that the coordination of nickel(II) ions to bidentate ligands of N-substituted 2-acetiminodimedone differs significantly from that in nickel(II) chelates of N-substituted salicylaldimines;³ therefore, we have studied nickel(II) chelates containing *N*- β -R,R'-aminoethyl-2-acetiminodimedone, abbreviated ac-Dim-en-N(R)R' (where dimedone is 5,5-dimethyl-1,3-cyclohexanedione), the tridentate ligand in structure B.



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The $\text{Ni}[\text{X-Sal-en-N}(\text{R})\text{R}']_2$ complexes are prepared by allowing bis(salicylaldehydato)nickel(II) dihydrate to react with the appropriate ethylenediamine. This is not applicable to the dimedone system due to the low solubility of bis(2-acetyldimedonato)nickel(II). Instead the Schiff base adduct of 2-acetyldimedone and an N-substituted ethylenediamine was prepared, and then it was treated with bis(tetraethylammonium)-tetrabromonickelate(II) in a procedure similar to the preparation of the bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes.³ The reaction yielded not only the anticipated $\text{Ni}[\text{ac-Dim-en-N}(\text{R})\text{R}']_2$ but also $\text{NiBr}[\text{ac-Dim-en-N}(\text{R})\text{R}']$.

The latter monohalo tridentate Schiff base complexes of nickel(II) ions are novel, there being no reports of comparable $\text{NiBr}[\text{X-Sal-en-N}(\text{R})\text{R}']$ compounds. Cationic species, such as $\text{NiCl}[(\text{C}_2\text{H}_5)_2\text{NCH}_2\text{CH}_2\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2]^+$, containing a nickel(II) ion bonded to a halide ion and a neutral tridentate ligand are known,⁴ but we present here the first report of a neutral monohalo tridentate nickel system.

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TABLE I
 CHARACTERIZATION OF SOME MONOHALO TRIDENTATE NICKEL(II) COMPLEXES

	Dec pt, ^a °C	% C		% H		% N		% X	
		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
NiBr[ac-Dim-en-N(CH ₃) ₂]									
Purple	200	43.12	43.12	5.95	5.77	7.18	7.24	20.49 ^b	20.54
Orange	230	43.12	42.76	5.95	5.73	7.18	7.29	20.49 ^b	20.55
NiCl[ac-Dim-en-N(CH ₃) ₂]	215-217	48.69	49.02	6.71	6.90	8.11	8.11	10.27 ^c	10.29
NiNCS[ac-Dim-en-N(CH ₃) ₂]	241-248	48.94	48.86	6.25	6.29	11.42	11.44	8.70 ^d	8.76
NiBr[ac-Dim-en-N(C ₂ H ₅) ₂]	165-170	45.92	46.18	6.46	6.49	6.70	6.74	19.14 ^b	19.25
NiBr[ac-Dim-NCH ₂ -α-py]	255-260	46.89	46.74	4.67	4.58	6.83	6.64	19.50 ^b	19.35
NiBr[ac-Dim-en-N(H)CH ₃]	247-250	41.53	41.56	5.63	6.02	7.45	7.44	21.26 ^b	21.03
NiBr[ac-Dim-en-N(H)CH ₃] CHCl ₃	240-243	38.95	38.95	4.48	4.21	5.66	5.64	16.13 ^b	16.16
NiBr[ac-Dim-en-N(H)C ₂ H ₅]	168-169	43.12	42.99	5.95	6.00	7.18	7.16	20.49 ^b	20.68
NiBr[ac-Dim-en-N(H)C ₂ H ₅] CHCl ₃	170-172	35.37	35.64	4.75	4.43	5.50	5.51	15.69 ^b	15.77
NiBr[formyl-Dim-en-N(CH ₃) ₂]	308-310	41.68	41.54	5.61	5.92	7.48	7.35	21.13 ^b	21.38
NiCl[formyl-Dim-en-N(CH ₃) ₂]	270	47.00	46.87	6.35	6.48	8.47	8.60	10.70 ^c	10.93
NiBr[formyl-Dim-en-N(C ₂ H ₅) ₂]	182-184	44.60	44.52	6.25	6.28	6.95	6.61	19.79 ^b	19.77

^a Uncorrected; complexes melt with decomposition. ^b Bromine. ^c Chlorine. ^d Sulfur.

Experimental Section

Preparation of Ligands.—2-Acetyldimedone was synthesized by the procedure of Smith⁵ and 2-formyldimedone by the procedure of Rogers and Smith.⁶ These dimedone derivatives were then treated with the appropriate ethylenediamine according to the method of Dudek and Volpp.⁷ The products were identified by their proton resonance spectra but were not further characterized.⁸

Preparation of Complexes.—All the complexes except the thiocyanato-*N* derivative were prepared by the following general method. The dried Schiff base (10⁻² mol) was added to sodium methoxide (1.1 × 10⁻² mol) in methanol, the sodium methoxide having been made *in situ* from sodium. The solution was heated with stirring to dissolve the ligand. The source of nickel(II) ions (1.5 × 10⁻² mol) was then added, it being either bis(tetraethylammonium)tetrabromonickelate(II) or nickel(II) bromide-1,2-dimethoxyethane for the bromo derivatives, the latter giving the better yield, and nickel(II) chloride-1,2-dimethoxyethane for the chloro derivatives. The reaction mixture was stirred for 2 hr at 40°. The methanol was removed by rotary evaporation and the complexes were extracted with hot toluene. The compounds were recrystallized from toluene except for the orange form of NiBr[ac-Dim-en-N(CH₃)₂] which precipitated from hot acetone on stirring and for the chloroform adducts which were recrystallized from chloroform-hexane. The yields of purified product ranged from 10 to 40%.

NiNCS[ac-Dim-en-N(CH₃)₂] was prepared by combining acetone solutions of the chloro analog (10⁻³ mol) and potassium thiocyanate (1.2 × 10⁻³ mol). After filtering off the potassium chloride precipitate, the acetone was evaporated and the crude product was recrystallized from toluene; yield 50%. The analytical data and decomposition temperatures are given in Table I.

Chemicals.—The nickel(II) bromide-1,2-dimethoxyethane and nickel(II) chloride-1,2-dimethoxyethane were supplied by Alfa Inorganics, Inc., and the chloroform-*d* was supplied by Merck Sharp and Dohme of Canada.

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer as Nujol mulls. Visible spectra of chloroform solutions were measured on a Perkin-Elmer 202 spectrophotometer. The chloroform was passed through a column of aluminum oxide immediately before use. A Cary 14 spectrophotometer was used to record the near-infrared spectra of the Nujol mulls.

Proton magnetic resonance spectra were run on a Varian A-60A spectrometer with a variable-temperature probe. Temperatures between 30 and 65° were calibrated with ethylene glycol. Chloroform-*d* was the solvent used, and tetramethylsilane (TMS) was the internal standard.

Magnetic measurements of solid samples were obtained with a Gouy balance or a Faraday balance. Mercury(II) tetrathio-

cyanatocobaltate(II) was the calibrant.⁹ Diamagnetic corrections were estimated from Pascal's constants,¹⁰ and the magnetic moments were calculated using the expression $\mu_{\text{eff}} = 2.84 \cdot (\chi_M T)^{1/2}$. Magnetic susceptibilities of solutions at room temperature were measured according to Evans' method using proton magnetic resonance.¹¹ The solvent was a 90% dried chloroform-10% tetramethylsilane (v/v) mixture. A precision coaxial capillary purchased from Wilmad Glass Co., Inc. Buena, N. J., was used for the reference solvent. Densities of the solvent and the solutions were estimated by averaging a number of volume measurements made with a micropipet.

Mass spectra were taken with an Associated Electrical Industries MS-9 instrument using a direct-insertion probe. Molecular weights in chloroform solutions were obtained with a Mechrolab osmometer, Model 302. The conductivity of 10⁻³ M solutions in 1,2-dichloroethane were recorded with an Industrial Instruments, Inc., conductivity bridge, Model RC-16B2. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Results

There is no evidence of ionization of the complexes in noncoordinating solvents. For 10⁻³ M solutions in 1,2-dichloroethane the recorded conductance of NiBr[ac-Dim-en-N(CH₃)₂] was 0.16 ohm⁻¹ cm² M⁻¹ while that of (C₂H₅)₄NBr was 23 ohm⁻¹ cm² M⁻¹. Molecular association of the same nickel complex in chloroform is small, 0.04 and 0.02 M solutions giving molecular weights of 418 ± 6 and 405 ± 6, respectively, whereas the calculated molecular weight is 390.

Infrared Spectra.—The infrared spectrum of a Nujol mull of NiNCS[ac-Dim-en-N(CH₃)₂] is indicative of Ni-NCS bonding. The two bands at 795 and 845 cm⁻¹ are in the 780-860-cm⁻¹ range of C-S stretching frequencies observed for thiocyanato-*N* compounds and above the 690-720 cm⁻¹ range attributed to thiocyanato-*S* derivatives.¹²

Mass Spectra.—The mass spectrum of each compound contained peaks corresponding to the molecular ion LNiX⁺ and the fragment LNi⁺. The two mono-substituted complexes NiBr[ac-Dim-en-N(H)R'] also displayed (L-H)Ni⁺ fragments and the dimeric cations (L-H)₂Ni₂⁺. At the high temperature (~200°) and low pressure (~10⁻⁶ mm) of the spectrometer, the spectra of the two chloroform adducts did not show any chloroform-containing fragments.

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The $\text{LNiX}^+/\text{LNi}^+$ and $(\text{L-H})_2\text{Ni}_2^+/\text{LNiX}^+$ intensity ratios declined somewhat as the temperature was increased; however, approximate values of the ratios are cited in Table II. The higher $\text{LNiX}^+/\text{LNi}^+$ values,

TABLE II
APPROXIMATE INTENSITY RATIOS OF ION FRAGMENTS

	$\text{LNiX}^+/\text{LNi}^+$	$(\text{L-H})\text{Ni}^+/\text{LNi}^+$	$(\text{L-H})_2\text{Ni}_2^+/\text{LNiX}^+$
$\text{NiBr}[\text{ac-Dim-NCH}_2\text{-}\alpha\text{-py}]$	0.3
$\text{NiX}[\text{ac-Dim-en-N}(\text{R})\text{R}']$			
R = H, R' = CH_3	0.7	1.2	0.05
R = H, R' = C_2H_5	0.8	1.0	0.10
R = R' = alkyl	~ 2.0
$\text{NiX}[\text{formyl-Dim-en-N}(\text{R})\text{R}']$	~ 5.0
R = R' = alkyl			

2.9 and 3.3 BM.¹⁴ The low values of 0.6–2.6 BM in Table III may result from association between planar monomers in the solid state producing a quasioctahedral coordination.^{15,16} The order of increasing magnetic moments would give the order of increasing association. The decline in solubility of the complexes does parallel the order of increasing magnetic moments. In fact the least soluble compound, $\text{NiBr}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$, has a moment in the range cited for octahedral nickel(II) complexes.¹⁴

Optical Spectra.—The spectra of all the chloroform solutions are characteristic of square-planar complexes with no detectable absorption below $15,000\text{ cm}^{-1}$ (see Table IV).¹⁷ For a given tridentate ligand, the fre-

TABLE III
MAGNETIC MOMENTS OF SOLID SAMPLES

	μ_{eff} , BM		μ_{eff} , BM
$\text{NiBr}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$		$\text{NiBr}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$	3.12
Purple	1.5	$\text{NiCl}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$	1.22
Orange	2.6	$\text{NiBr}[\text{formyl-Dim-en-N}(\text{C}_2\text{H}_5)_2]$	Diamag
$\text{NiCl}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$	0.66	$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{CH}_3]$	Diamag
$\text{NiNCS}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$	Diamag	$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{CH}_3] \cdot \text{CHCl}_3$	3.25
$\text{NiBr}[\text{ac-Dim-en-N}(\text{C}_2\text{H}_5)_2]$	Diamag	$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{C}_2\text{H}_5]$	Diamag
$\text{NiBr}[\text{ac-Dim-NCH}_2\text{-}\alpha\text{-py}]$	Diamag	$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{C}_2\text{H}_5] \cdot \text{CHCl}_3$	3.28

TABLE IV
LIGAND FIELD SPECTRA^a

	Medium	ν_{max} , cm^{-1} (ϵM) ^b		
$\text{NiBr}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$	CHCl_3	18,900 (230)		
$\text{NiCl}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$	CHCl_3	19,400 (260)		
$\text{NiNCS}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$	CHCl_3	20,400 (420)		
$\text{NiBr}[\text{ac-Dim-en-N}(\text{C}_2\text{H}_5)_2]$	CHCl_3	18,700 (205)		
$\text{NiBr}[\text{ac-Dim-NCH}_2\text{-}\alpha\text{-py}]$	CHCl_3	19,200 (230)		
$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{CH}_3]$	CHCl_3	19,600 (370)		
$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{C}_2\text{H}_5]$	CHCl_3	19,600 (250)		
$\text{NiBr}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$	CHCl_3	18,800 (215)		
$\text{NiCl}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$	CHCl_3	19,200 (225)		
$\text{NiBr}[\text{formyl-Dim-en-N}(\text{C}_2\text{H}_5)_2]$	CHCl_3	18,700 (275)		
$\text{NiBr}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$				
Purple	Nujol	18,200 (1.0)	11,200 (0.51)	8300 (0.42)
Orange	Nujol	21,000 (1.6)	13,400 (1.0)	11,100 (0.58)
$\text{NiBr}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$	Nujol	16,100 (1.0)	10,800 (0.9)	
$\text{NiCl}[\text{formyl-Dim-en-N}(\text{CH}_3)_2]$	Nujol	19,400 (1.0)	11,200 (0.25)	
$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{CH}_3] \cdot \text{CHCl}_3$	Nujol	15,600 (0.58)	12,700 (0.73)	7700 (0.85)
$\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{C}_2\text{H}_5] \cdot \text{CHCl}_3$	Nujol	15,600 (0.63)	12,700 (0.79)	7700 (0.83)

^a All obtained at room temperature. ^b Relative intensities cited for Nujol mulls.

for the disubstituted as compared with monosubstituted analogs, may be due to a greater stabilizing of the tricoordinate nickel in the LNi^+ ion by the monosubstituted ligands. High-mass species $(\text{L-H})_2\text{Ni}_2^+$ have been reported for $\text{Ni}[\text{Sal-en-N}(\text{H})\text{R}']_2$ complexes but at a considerably higher relative intensity. For $\text{Ni}[\text{Sal-en-N}(\text{H})\text{CH}_3]_2$, the $(\text{L-H})_2\text{Ni}_2^+/\text{L}_2\text{Ni}^+$ intensity ratio is about 1.0.¹⁸

Magnetic Data.—The magnetic moments of solid samples are listed in Table III. The diamagnetism is suggestive of a square-planar orientation for the nickel-ligand bonding. The moments of 3.2 BM for the two chloroform adducts are in the range of the values 3.2–3.4 BM, recorded for high-spin, five-coordinate complexes of nickel(II).¹⁴ Six-coordinate, octahedral nickel(II) complexes have magnetic moments between

quency of the band decreases in the order $\text{NCS} > \text{Cl} > \text{Br}$, the normal sequence for the spectrochemical series. For a given X group, the frequency is essentially the same for analogous acetyl and formyl derivatives. Variation of the R and R' groups shifts the absorption maximum a little, the shift being toward lower energies with increased substitution: $\text{N}(\text{H})\text{CH}_3 \geq \text{N}(\text{H})\text{-C}_2\text{H}_5 > \text{N}(\text{CH}_3)_2 \geq \text{N}(\text{C}_2\text{H}_5)_2$. This is the same order reported by Sacconi and Bertini for $\text{CuCl}[\text{Sal-en-N}(\text{R})\text{R}']$ complexes.¹⁸

The spectra of mull samples and chloroform solutions are identical with five notable exceptions. For NiBr -

(15) The paramagnetism may be due to the thermal population of a low-lying triplet state (see ref 16). An investigation into the variation of the magnetic moments with temperature for the solid samples would be of interest, but no appropriate instrumentation was available.

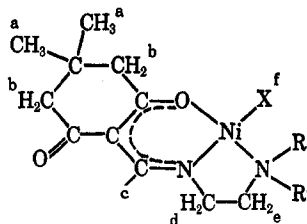
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TABLE V
CHEMICAL SHIFT DATA^a

	a	b	c	d	e	f	Resonances
H[ac-Dim-en-N(CH ₃) ₂]	1.03	2.36	2.58 (CH ₃)	3.47 q ^b	2.58	13.5	2.30 (CH ₃)
NiBr[ac-Dim-en-N(CH ₃) ₂]							
0.10 <i>m</i>	0.99	2.25	2.05 (CH ₃)	5.54	4.07	...	5.32 (CH ₃)
0.05 <i>m</i>	0.95	2.23	2.26 (CH ₃)	4.26	3.00	...	3.81 (CH ₃)
NiCl[ac-Dim-en-N(CH ₃) ₂]	0.99	2.31	2.37 (CH ₃)	3.99	2.85	...	3.48 (CH ₃)
NiNCS[ac-Dim-en-N(CH ₃) ₂]	0.97	2.27, 2.36	2.44 (CH ₃)	3.99 t	2.4	...	2.62 (CH ₃)
H[ac-Dim-en-N(C ₂ H ₅) ₂]	0.90	2.12	2.41 (CH ₃)	3.32 q	2.5	13.0	2.49 q (CH ₂) 0.90 t (CH ₂) 2.8 } (CH ₂) 3.49 } 1.85 t (CH ₃)
NiBr[ac-Dim-en-N(C ₂ H ₅) ₂]	0.90	2.19	2.33 (CH ₃)	3.49	2.64	...	2.49 (CH) (H not detected)
H[ac-Dim-en-N(H)CH ₃]	1.03	2.35	2.57 (CH ₃)	3.53 q	2.88	13.1	4.10 (CH ₂) (H not detected)
NiBr[ac-Dim-en-N(H)CH ₃]	0.95	2.26	2.31 (CH ₃)	3.66	2.78	...	2.85 (CH ₂) 1.20 t (CH ₃) (H not detected)
H[ac-Dim-en-N(H)C ₂ H ₅]	1.10	2.15	2.44 (CH ₃)	3.35	2.85	13.0	4.15 (CH ₂) 1.99 t (CH ₃) (H not detected)
NiBr[ac-Dim-en-N(H)C ₂ H ₅]	0.99	2.30	2.40 (CH ₃)	4.0	2.7	...	8.6-8.7 ortho ^c 7.2-7.3 meta ^c 7.7 para ^c 9.5 ortho ^c 7.4 meta ^c 7.7 para ^c
H[ac-Dim-NCH ₂ -α-py]	1.04	2.39	2.63 (CH ₂)	4.75 d	...	23.3	2.29 (CH ₃)
NiBr[ac-Dim-NCH ₂ -α-py]	0.97	2.33	2.46 (CH ₃)	5.07	
H[formyl-Dim-en-N(CH ₃) ₂]	1.04	2.19, 2.24	8.0 d (H)	3.50 q	2.52 t	9.3	
NiCl[formyl-Dim-en-N(CH ₃) ₂]							
0.5 <i>m</i>	1.00	2.18, 2.27	(H not detected)	4.68	3.60	...	4.25 (CH ₃)
H[formyl-Dim-en-N(C ₂ H ₅) ₂]	1.01	2.16, 2.21	8.0 d (H)	3.62	2.55	9.3	2.55 (CH ₂) 1.01 t (CH ₃)
NiBr[formyl-Dim-en-N(C ₂ H ₅) ₂]	0.95	2.21	9.77 (H)	3.80	2.54 t	...	2.91 } (CH ₂) 3.80 } 1.90 t (CH ₃)

^a Chemical shifts of CDCl₃ solutions measured in ppm from an internal standard, tetramethylsilane. Solutions of the complexes are 0.1 *m* unless otherwise indicated. ^b Abbreviations: q, quartet; t, triplet; d, doublet. ^c With reference to nitrogen.

[formyl-Dim-en-N(CH₃)₂] two bands of almost equal intensity at 10,800 and 16,100 cm⁻¹ are consistent with an octahedral structure, the transitions being ³A_{2g} → ³T_{2g} and ³A_{2g} → ³T_{1g}(F), respectively, based on O_h symmetry. The 11,200-cm⁻¹ band exhibited by NiCl[formyl-Dim-en-N(CH₃)₂] is indicative of some intermolecular association, as are the low-intensity absorptions recorded for the two solid forms of NiBr[ac-Dim-en-N(CH₃)₂]. In the resulting tetragonal structure of D_{4h} symmetry, the lower energy transition, ³A_{2g} → ³T_{2g}, of an octahedral form may be split into two components, ³B_{1g} → ³E_g and ³B_{1g} → ³B_{2g}. The 8300- and 11,200-cm⁻¹ bands in the spectra of NiBr[ac-Dim-en-N(CH₃)₂] are assigned to these two transitions, respectively.

The spectrum of each of the two chloroform adducts contains four bands similar to the spectrum reported for Ni[5-Cl-Sal-en-N(C₂H₅)₂]₂.² This compound of an irregular square-pyramidal structure^{19,20} exhibits absorptions at 7500, 9900, 12,600, and 16,500 cm⁻¹ which have

(19) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Amer. Chem. Soc.*, **87**, 2059 (1965).

(20) P. L. Orioli, M. Di Vaira, and L. Sacconi, *ibid.*, **88**, 4383 (1966).

been assigned to transitions from the ³B₁ ground state to the ³E, ³A₂, ³B₂, and ³E states, respectively, assuming C_{4v} symmetry.²¹ Thus the chloroform adducts are most likely five-coordinate, but the structure of square pyramidal *vs.* trigonal bipyramidal cannot be established on the basis of the optical spectra, since the transitions are dependent upon internal bond angles, and neither C_{4v} nor D_{3h} symmetry is attained due to differences in the coordinating atoms.

Proton Magnetic Resonance.—The pmr data for the complexes and corresponding ligands are compiled in Table V. The resonance of the CH₂ group adjacent to the α nitrogen is a quartet (*J* ≈ 7 Hz) in all the spectra of the free ligands except for H[ac-Dim-NCH₂-α-py] where it is a doublet. The formyl proton appears as a doublet in the ligand spectra (*J* = 14 Hz when R = R' = CH₃ and *J* = 11 Hz when R = R' = C₂H₅) but is a singlet in the complexes. The multiplet structure of the N_αCH₂ protons and of the formyl proton indicate that the principal enantiomer of the free ligands is the keto amine form with a proton on the α nitrogen. This

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proton experiences strong hydrogen bonding as shown by the large downfield chemical shift, the shift increasing in the order $H[\text{formyl-Dim-en-N(R)R}'] < H[\text{ac-Dim-en-N(R)R}'] < H[\text{ac-Dim-NCH}_2\text{-}\alpha\text{-py}]$.

When the Schiff base is bonded to the NiX group, the resonance of the amide proton is absent. The multiplet bands are broadened due presumably to paramagnetism produced by some solute association. Consequently peak assignments are based not on multiplet structure but on relative intensities with the broadest resonance for a given intensity being attributed to the group nearest to the coordinating nitrogen atoms. For the two CH_2 resonances of the ethylene moiety, the one at lower field is assigned to the CH_2 group bonded to the α nitrogen in order to parallel the unequivocal chemical shifts of the ethylene group in the free ligands and in keeping with the relatively low-field position of the NCH_2 resonance of the $\text{NiBr}[\text{ac-Dim-NCH}_2\text{-}\alpha\text{-py}]$ complex. The assignment of the three low-field CH_2 resonances of the complex $\text{NiBr}[\text{ac-Dim-en-N(H)C}_2\text{H}_5]$ was made by a comparison with the $R = R' = \text{CH}_3$ derivatives for which the chemical shift of the $\text{CH}_2\text{N}_\beta$ resonance is less than 4.0 ppm for tetramethylsilane and is generally about 2.5 ppm. The band assignment for the $R = R' = \text{C}_2\text{H}_5$ derivatives is less certain because four CH_2 resonances appear at fields below 2.5 ppm. Of the four resonances, the one at highest field (at about 2.6 ppm), which is split into a triplet for the compound $\text{NiBr}[\text{formyl-Dim-en-N(C}_2\text{H}_5)_2]$, is most likely due to the $\text{CH}_2\text{N}_\beta$ group of the ethylene moiety. The two lowest field resonances appear as overlapping bands which are separated by the addition of about 10% by volume of benzene to the chloroform solution. Since, in all other compounds, the $\text{N}_\alpha\text{CH}_2$ resonance is shifted downfield upon coordination with the NiX group, one of the overlapping bands has been attributed to this $\text{N}_\alpha\text{CH}_2$ group. The two intermediary CH_2 resonances have been assigned to the CH_2 groups of the $R = R' = \text{C}_2\text{H}_5$ substituents. The cause of this unexpected nonequivalence in the two C_2H_5 groups is being investigated by studying similar monohalo tridentate chelates of nickel(II), and our conclusions will be discussed in a later paper.

The pmr bands of the R and R' substituents and the $\text{N}_\alpha\text{CH}_2$ group in a complex are shifted downfield significantly from the corresponding resonance positions of the free ligand. In the acetyl derivatives, however, the acetyl CH_3 peak moves a little upfield while the formyl proton resonance in $\text{NiBr}[\text{formyl-Dim-en-N(C}_2\text{H}_5)_2]$ moves to a considerably lower field. The magnitude of these shifts increases with an increase in concentration and with a decrease in temperature. The temperature and concentration dependence is more pronounced for the less soluble derivatives.

The magnetic moment of $\text{NiBr}[\text{ac-Dim-en-N(CH}_3)_2]$ in chloroform solutions increases with concentration. The estimated error of the values listed in Table VI is $\pm 5\%$. For less concentrated solutions, the inaccuracy is larger due to the uncertainty in the smaller chemical shift differences between the two tetramethylsilane signals (less than 2 Hz) and to the uncertainty in the density-concentration factor $(d_o - d_s)/m$ (where d_o and d_s are the densities of the solvent and solution, respectively, and m is the mass of solute per liter of solution), a factor which increases with dilution.

The increase in paramagnetism of $\text{NiBr}[\text{ac-Dim-en-}$

TABLE VI
PMR CHEMICAL SHIFT (PPM) OF $\text{NiBr}[\text{ac-Dim-en-N(CH}_3)_2]$
COMPARED WITH THE RESONANCE OF THE
FREE LIGAND AND MAGNETIC DATA

[CDCl ₃ soln], m	$\Delta[\text{acetyl CH}_3]$	$\Delta[\text{N}_\alpha\text{CH}_2]$	$\Delta[\text{CH}_2\text{N}_\beta]$	$\Delta[\text{N(CH}_3)_2]$	μ_{eff}^a BM
0.010	0.21	-0.12	0.13	-0.65	...
0.025	0.25	-0.29	0.04	-0.90	...
0.034	0.27	-0.47	-0.15	-1.11	...
0.065	0.37	-1.12	-0.69	-1.91	0.76
0.104	0.53	-2.07	-1.49	-3.02	0.87
0.215	1.16	-6.30	-4.78	-7.47	0.99
Temp, °C	1/T × 10 ³ , °K ⁻¹	$\Delta[\text{N(CH}_3)_2]$	Temp, °C	1/T × 10 ³ , °K ⁻¹	$\Delta[\text{N(CH}_3)_2]$
26.5	3.34	-5.25	61.0	3.00	-3.25
46.0	3.13	-3.95	72.0	2.90	-2.92

^a Magnetic moments measured by Evans' method.¹¹

$\text{N(CH}_3)_2]$ with concentration is most likely due to an association between the planar, diamagnetic molecules of the nickel(II) chelate producing a paramagnetic, octahedral form. The changes in resonance positions are then isotropic contact shifts of the paramagnetic species.²² The downfield shifts are in the direction expected for spin delocalization in the σ system, but the opposite sign of the formyl and acetyl shifts is indicative of some polarization in the π -spin density. The downfield shift of the $\text{N}_\alpha\text{CH}_2$ group may also be due to spin imbalance in the lowest filled π molecular orbital of the odd-alternating ligand system.²³ Spin transferred by the ligand π orbitals has been reported for the bidentate complexes bis(N-substituted 2-acetimidodimedonato)-nickel(II).³ To summarize, chemical shift data in Table V are suggestive of some π transmission of spin density in the conjugated six-membered chelate ring, whereas the shifts of the groups bound to the N_β nitrogen may be produced by only a σ transmission of spin density.

If the temperature and concentration dependence of the chemical shifts is due to association between solute molecules, the magnitude of the effect is a qualitative measure of the relative amount of association. According to the pmr data, the association increases in the order $\text{NiNCS}[\text{ac-Dim-en-N(CH}_3)_2] \approx \text{NiBr}[\text{ac-Dim-en-N(C}_2\text{H}_5)_2] < \text{NiBr}[\text{ac-Dim-NCH}_2\text{-}\alpha\text{-py}] \lesssim \text{NiBr}[\text{formyl-Dim-en-N(C}_2\text{H}_5)_2] \lesssim \text{NiBr}[\text{ac-Dim-en-N(H)C}_2\text{H}_5] \lesssim \text{NiBr}[\text{ac-Dim-en-N(H)CH}_3] \lesssim \text{NiCl}[\text{ac-Dim-en-N(CH}_3)_2] \ll \text{NiBr}[\text{ac-Dim-en-N(CH}_3)_2] < \text{NiCl}[\text{formyl-Dim-en-N(CH}_3)_2]$ with $\text{NiBr}[\text{formyl-Dim-en-N(CH}_3)_2]$ being too insoluble in chloroform for a measurable pmr spectrum.

The chemical shifts of $\text{NiBr}[\text{ac-Dim-en-N(CH}_3)_2]$ were extensively investigated since the spectra of this compound were strongly temperature and concentration dependent, yet the compound was sufficiently soluble for resonances to be detected over a 40° temperature range and over a 0.2–0.02 *m* concentration change. Representative data are given in Table VI. The change in the shift of the $\text{N(CH}_3)_2$ resonance per molal concentration change decreases with dilution. The shift approaches a limiting value of -0.6 ppm which presumably is the resonance position of the monomeric species. The thiocyanato analog, which shows no concentration shifts, has a corresponding value of -0.3 ppm. Contact shifts are linearly dependent on $1/T$ (°K) for an assembly of paramagnetic complexes

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with the same ground state such as a single, fully associated octahedral form. Deviation from linearity is indicative of the formation of some other species.²² In this study the variation of the shifts with $1/T$ decreases at higher temperatures as expected if the relative amount of diamagnetic monomer increases with temperature.

Conclusions

The magnetic and spectral data indicate a variable amount of intermolecular association in the monohalo tridentate nickel(II) complexes of this study. Changing the halo group decreases the association in the order $\text{Br} > \text{Cl} > \text{NCS}$. This follows the spectrochemical series and suggests that the stronger the ligand-nickel bonding within a molecule, the weaker the interaction between molecules.

It also parallels the tendency of these groups to form M-X-M bonds. The intermolecular association may well be through weak Ni-X-Ni links, the most polarizable X group, bromine, giving the strongest bridge. Attempts to prepare an iodo derivative failed. According to the mass spectrum, some $\text{NiI}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$ had been prepared, but it was too insoluble to be separated from nickel(II) iodide.

Compared with the role of the halo group, modifying the tridentate ligand has only a small effect on the ligand field spectra but a large effect on the intermolecular association. Due presumably to steric interactions, the association is decreased by replacing two CH_3 groups on the β nitrogen by two C_2H_5 groups and by substituting a CH_3 group for the formyl proton. A comparable change has been reported by Kannan and Chakravorty for $\text{Ni}[\text{Sal-N}(\text{R})_2]$ compounds.²⁴ Introduction of a CH_3 group for the aldehyde proton lessens the amount of molecular aggregates in the solution phase. One of the more associated complexes of this study, $\text{NiBr}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$, seems to exhibit a varying amount of association in the solid state existing in two forms with the distinction between forms vanishing in chloroform solution.

The association does not parallel the steric factor entirely since $\text{NiBr}[\text{ac-Dim-en-N}(\text{H})\text{CH}_3]$ is more soluble, has a lower magnetic moment, and shows smaller proton contact shifts than $\text{NiBr}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$. The relatively small association of the two monosubstituted complexes may be attributed to the stronger ligand-metal bonding depicted in the ligand field spectra, but in chloroform solutions solute-solvent interaction also contributes. The two monosubstituted complexes and only these yield solid 1:1 complex-chloroform adducts when recrystallized from chloroform-hexane. Most likely the chloroform is associated through the hydrogen on the β nitrogen.

The nature of the R and R' substituents on the β nitrogen limits the number of $\text{NiX}[\text{ac-Dim-en-N}(\text{R})\text{R}']$ complexes. Sacconi and Bertini reported that for $\text{Sal-en-N}(\text{R})\text{R}'$ ligands the donor capacity of the β nitrogen increases in the order $\text{N}(\text{H})\text{C}_6\text{H}_5 < \text{N}(\text{C}_2\text{H}_5)_2 < \text{N}(\text{CH}_3)_2 < \text{N}(\text{H})\text{CH}_3$ with the size of the amino group prevailing over the basicity.¹⁸ Apparently the $\text{NiX}[\text{ac-Dim-en-N}(\text{R})\text{R}']$ compounds must contain tridentate ligands with relatively strongly coordinating β nitrogens, because we could not prepare the $\text{R} = \text{H}$, $\text{R}' = \text{C}_6\text{H}_5$ and the $\text{R} = \text{R}' = i\text{-C}_3\text{H}_7$ analogs. The pyridine derivative exists, for although pyridine is a

weak base, it offers small steric interaction and electron delocalization *via* back- π -bonding. The ligand field spectrum, the low value of the $\text{LNiX}^+/\text{LNi}^+$ intensity ratio, and the relatively small degree of intermolecular association indicate that the pyridine-containing ligand is strongly bound to the nickel(II) ion.

The greater stability of five-membered saturated metal-chelate rings compared with analogous six-membered rings is illustrated by our findings. According to mass spectral data, the complex $\text{NiBr}[\text{ac-Dim-N}(\text{CH}_2)_3\text{N}(\text{CH}_3)_2]$ had been prepared, but on subsequent recrystallizations it decomposed.

We have failed to prepare monohalo tridentate nickel(II) complexes with an adduct of *N,N*-dimethylethylenediamine and either 2,4-pentanedione or 3-benzyl-2,4-pentanedione. Analogous nickel(II) complexes which we have synthesized from adducts of salicylaldehyde and substituted ethylenediamines exhibit the correct molecular ions in the mass spectra but have low solubility and unique spectral and magnetic properties which we are currently investigating.

Why do the dimedone derivatives form monohalo tridentate nickel(II) compounds more readily than β -keto amines or salicylaldimines? Our study of bidentate bis(*N*-substituted 2-acetiminodimedonato)nickel(II) chelates indicates that dimedone promotes a planar configuration and hinders molecular association in comparison with analogous (β -keto amine)- and salicylaldiminenickel(II) complexes. Strong coordinate bonding in the dimedone chelates of nickel(II) as depicted by relatively high-energy ligand field bands (*e.g.*, $\text{Ni}[\text{ac-Dim-N-}o\text{-C}_6\text{H}_4\text{CH}_3]_2$, 20,500 and 18,000 cm^{-1} ; $\text{Ni}[\text{CH}_3\text{COCHC}(\text{CH}_3)\text{N-}o\text{-C}_6\text{H}_4\text{CH}_3]_2$, 20,500 and 16,450 cm^{-1} ;²³ and $\text{Ni}[\text{Sal-N-}o\text{-C}_6\text{H}_4\text{CH}_3]_2$, 16,300 cm^{-1} ;²⁵ all three complexes being planar in chloroform solution) most likely fosters the planar form. Apparently the monohalo tridentate nickel(II) complexes require strong ligand-nickel coordination including a β nitrogen of high donor strength. For the nickel(II) chelates containing the dimedone moiety, the relatively low intermolecular association, most likely due to the steric interference of the 5,5-dimethyl group and the nonplanar dimedone ring and to the stronger intramolecular coordinate bonding, facilitates the synthesis of the monohalo tridentate complexes.

It is significant that the monohalo tridentate nickel(II) chelates are a potential source of many interesting nickel(II) complexes prepared *via* exchange of the halo group. The compound $\text{NiNCS}[\text{ac-Dim-en-N}(\text{CH}_3)_2]$, was prepared by exchange of a chloro group for the thiocyanato substituent. We find that a halo moiety may be replaced by a bidentate (1-) anion to yield a neutral, five-coordinate nickel(II) species. The usefulness of such halo-exchange reactions will be reported subsequently.

Acknowledgment.—We thank Dr. Gerald O. Dudek, Harvard University, for helpful suggestions and for recording the mass spectra. We are indebted to Professor Richard H. Holm, Massachusetts Institute of Technology, for the use of a Faraday balance and to Gareth R. Eaton for assisting us in operating the balance. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for this research.

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