above, 348 mg (1.05 mmol) of π-cyclopentadienyl-σ-methyl(tri-*n*-butylphosphine)nickel (**13**)[6] and *ca.* 15 ml of liquid sulfur dioxide afforded 143 mg (30% yield) of **15** as green crystals, mp 77.5–78°. *Anal.* Calcd for $C_{27}H_{29}NiO_2PS$: C, 53.35; H, 8.71; P, 7.65; S, 7.81. Found: C, 53.20; H, 8.67; P, 7.68; S, 7.90.

Acknowledgments.—The authors are indebted to the National Science Foundation for a grant in support of this research program and to Dr. M. Strem for providing a sample of bis(π-cyclopentadienyl)dicarbonyldinickel.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
WELLESLEY COLLEGE, WELLESLEY, MASSACHUSETTS

Bidentate Bis(N-substituted 2-acetiminodimedonato)nickel(II) Complexes

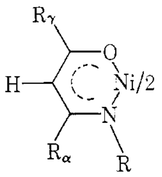
BY SANDRA Y. SHAW AND EMILY P. DUDEK[1]

Received December 9, 1968

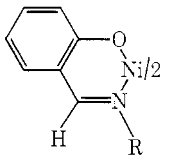
Bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes, where the substituent (R) is H, CH_3, *i*-C_3H_7, *sec*-C_4H_9, C_6H_5, *o*-$C_6H_4CH_3$, *p*-$C_6H_4CH_3$, or $C_6H_5CHCH_3$, have been synthesized and their magnetic and spectral properties investigated. All of the complexes are predominantly planar in the solid phase, and all but the three α-branched alkyl derivatives are planar in chloroform solution. The α-branched alkyl complexes exhibit a planar–tetrahedral equilibrium in solution with the amount of tetrahedral form less than 10% at room temperature and increasing in the order $C_6H_5CHCH_3 <$ *sec*-$C_4H_9 <$ *i*-C_3H_7. Analysis of the temperature dependence of the proton contact shifts has yielded $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the configurational interconversion. In comparison to analogous β-ketoamine– and salicylaldimine–nickel(II) complexes, dimedone promotes a planar configuration and hinders molecular association.

Introduction

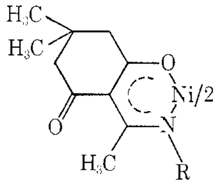
Nickel(II) complexes of bidentate N-substituted β-ketoamines (A) and salicylaldimines (B) have been widely investigated.[2-5] Two types of equilibria have been reported: (1) between planar monomeric species and associated, quasioctahedral forms, the association being either solute–solute or solute–solvent, and (2) between planar and tetrahedral configurations. In general the salicylaldimines favor the associated and planar forms more than the β-ketoamine derivatives do.



A



B



C

Bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes (C) (dimedone = 5,5-dimethyl-1,3-cyclohexanedione) offer an important extension to the study, because the ligand has a conjugated chelate ring comparable to that of A and B and yet it contains a nonaromatic ring instead of the straight chain of A or the aromatic ring of B. Such perturbations of the ligand "backbone" may affect significantly the stereochemistry of the nickel complexes. In a preliminary investigation, we found that the dimedone system appears to promote a nonassociated, planar configuration about the nickel ion.[6]

The selection of nitrogen substituents in our study of complexes of type C includes R = CH_3, α-branched *sec*-alkyl groups, and aryl moieties,[7] since it has been reported[2,3,8] that in A and B complexes branching of an alkyl group at the carbon adjacent to nitrogen enhances the per cent of tetrahderal form while the R = aryl complexes exhibit some molecular associations. The order of association is *o*-$C_6H_4CH_3$ > *p*-$C_6H_4CH_3$ for the A compounds and *o*-$C_6H_4CH_3$ < *p*-$C_6H_4CH_3$ for the B compounds. Because the planar–tetrahedral equilibrium displayed by complexes A and B is affected by the configuration at asymmetric ligand centers,[2,9] two ligands chosen for this study have optically active centers.

Experimental Section

Preparation of Ligands.—2-Acetyldimedone was synthesized by the procedure of Smith.[10] The N-substituted 2-acetiminodimedone ligands were prepared by treating the appropriate primary amine with 2-acetiminodimedone according to the method of Dudek and Volpp.[11] The products were purified by crystallization and were identified by their proton resonance spectra;[12] they were not further characterized.

Preparation of Complexes.—Complexes were prepared by a

---

[1] Department of Chemistry, Brandeis University, Waltham, Mass. 02154.

[2] R. H. Holm, G. W. Everett, Jr., and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 83 (1966).

[3] L. Sacconi, *Coord. Chem. Rev.*, **1**, 126 (1966).

[4] L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

[5] S. Yamada, *Coord. Chem. Rev.*, **1**, 415 (1966).

[6] S. McKinley and E. P. Dudek, *Inorg. Nucl. Chem. Letters*, **3**, 561 (1967).

[7] Complexes with R = *n*-alkyl and *t*-butyl were too hydrolytically unstable to be isolated.

[8] G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **87**, 2117 (1965).

[9] R. E. Ernst, M. J. O'Connor, and R. H. Holm, *ibid.*, **89**, 6104 (1967), and references cited therein.

[10] H. Smith, *J. Chem. Soc.*, 803 (1953).

[11] G. O. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).

[12] G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.*, **84**, 2691 (1962); G. O. Dudek and G. P. Volpp, *ibid.*, **85**, 2697 (1963).

TABLE I

CHARACTERIZATION OF BIS(N-SUBSTITUTED 2-ACETIMINODIMEDONATO)NICKEL(II) COMPLEXES

R	Mp,[a] °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
H	251	57.30	57.49	6.73	6.63	6.68	6.98
CH_3 (brown)	Turns blue about 100°						
(blue)	286–288	59.08	59.57	7.21	7.67	6.26	6.51
i-C_3H_7	239–240	62.04	61.81	7.99	7.91	5.57	5.75
sec-C_4H_9	218–220	63.29	63.02	8.35	8.16	5.27	4.96
C_6H_5	298–300	67.28	67.54	6.35	6.28	4.90	4.98
o-$C_6H_4CH_3$	293–295	68.12	68.09	6.74	7.04	4.67	4.69
p-$C_6H_4CH_3$	318–320	68.12	67.95 68.06	6.74	6.90 7.01	4.67	4.65
$C_6H_5CHCH_3$ (racemic)	202–204[b]	68.91	68.71	7.08	6.91	4.47	4.39

[a] Uncorrected. [b] For optically active form, mp 209–212°.

modification of the method of Everett and Holm.[8,13] Solid reagents were dried for 24 hr *in vacuo* over phosphorus pentoxide. As a consequence of the hydrolytic instability of the complexes, the reactions were carried out in dried *t*-butyl alcohol in a drybag. Potassium *t*-butoxide and the N-substituted 2-acetiminodimedone ligand were dissolved in the alcohol with stirring and heating at about 50°. Then bis(tetraethylammonium)tetrabromonickelate(II) was added and the mixture was stirred for 1–4 hr before the solvent was removed by lyophilization. The complexes were extracted with toluene and recrystallized from toluene. Yields of purified complexes ranged from 10 to 80%. The compounds are purple save for that where R = H which is bright red and that for R = CH_3 which was isolated in two forms, brown and blue.[6] The analytical data are reported in Table I.

Chemicals.—Chloroform-*d* was supplied by Merck Sharp and Dohme of Canada. The calibrant for magnetic susceptibility measurements, mercury(II) tetrathiocyanatocobaltate(II), was obtained from Eastman Organic Chemicals. The optically active (+)-*sec*-butylamine was generously contributed by Dr. G. O. Dudek while the (−)-α-methylbenzylamine was purchased from Fluka of Switzerland.

Electronic Spectra.—The near-infrared region was scanned on a Cary 14. Ultraviolet and visible spectra were recorded on a Perkin-Elmer 202. Samples were dissolved in dried chloroform. Path lengths were varied between 2 cm and 0.1 mm to avoid inaccuracies introduced by both dilution and hydrolysis from moisture contained in solvents. All spectra were recorded at room temperature.

Nuclear Magnetic Resonance.—Nuclear magnetic resonance spectra were run on a Varian A-60 with a variable-temperature probe. Temperatures below room temperature were calibrated with methanol. Readings between 30 and 65° were calibrated with ethylene glycol. Spectra were calibrated using an audiooscillator which was continually monitored by a frequency counter. Tetramethylsilane (TMS) was used as an internal standard. A solution (0.40 ml) of dried chloroform-*d* and TMS was added to the complex in the sample tube. The tubes were evacuated, sealed, and stored in liquid nitrogen to minimize decomposition. The spectrum of the complex where R = $C_6H_5CHCH_3$ was also recorded on a Varian HA-100.

Magnetic Susceptibility.—Magnetic measurements of solid samples were obtained by the Gouy method at room temperature (24 ± 2°). The calibrant was mercury(II) tetrathiocyanatocobaltate(II).[14] The magnetic moments were corrected for diamagnetic contributions using Pascal's constants.[15] Because of the error in measuring small weight changes for the weakly paramagnetic substances, because small amounts of paramagnetic impurities could contribute significantly to the low magnetic moments, and because the diamagnetic corrections are a large per cent of the small molar susceptibility values, the error may be as large as 0.2 BM (Bohr magneton) where $\mu_{eff} < 1$ BM.

Magnetic susceptibilities of solutions were measured according to Evans' method using nuclear magnetic resonance.[16] A solution of 90% dried chloroform–10% tetramethylsilane (v/v) was prepared in a drybag. About 0.1 ml of the solvent mixture was sealed in a melting point capillary. The sealed capillary and 0.40 ml of the solution were added to the weighed complex in a nuclear magnetic resonance sample tube. The tube was evacuated, sealed, and stored in liquid nitrogen. The spectra were recorded at several temperatures between 30 and 65°. The densities of the solvent mixture and of the solutions were estimated with a pycnometer.

Optical Activity.—A Perkin-Elmer Model 141 automatic polarimeter was used to obtain data at 578 mμ. One-decimeter cells were employed.

Results and Discussion

Electronic Spectra.—The ligand field spectral data are presented in Table II. Owing to some decomposition, the optical data are considered somewhat less accurate for the R = *i*-C_3H_7, *sec*-C_4H_9, and $C_6H_5CHCH_3$ complexes than for the other chelates.

For all chloroform solutions, no absorptions were recorded in the near-infrared region (15,000–6000 cm^{-1}) indicating that the per cent tetrahedral or associated species is sufficiently low at room temperature to be undetectable by optical measurements. The two absorptions in the visible spectra or the single, more intense band which is presumably the envelope of two bands is characteristic of a planar structure, the proposed band assignment being ${}^1A_g \rightarrow {}^1B_{1g}$ for the lower energy transition and ${}^1A_g \rightarrow {}^1B_{3g}$ for the second transition based on D_{2h} microsymmetry.[17]

The R = CH_3 derivative exists in two forms in the solid state, a brown form which is converted into a blue species upon heating to about 100°. The weak near-infrared absorption of the blue form suggests that it is a polymer of the brown, planar species.[6,18]

---

(13) G. W. Everett, Jr., and R. H. Holm, *Proc. Chem. Soc.*, 238 (1964).

(14) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 190 (1958).

(15) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1943, pp 51–53.

(16) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).

(17) S. Yamada, H. Nishikawa, and E. Yoshida, *Bull. Chem. Soc. Japan*, **39**, 994 (1966).

(18) Crystal data obtained by T. A. O'Brien and M. R. Churchill are: brown: Pbca, orthorhombic, $Z = 4$, unit cell volume 2248 Å^3, $a = 7.470$ Å, $b = 10.34$ (1) Å, $c = 29.10$ (6) Å, $\alpha = \beta = \gamma = 90°$; blue: Pbca, orthorhombic, $Z = 4$, unit cell volume 2369 Å^3, $a = 9.32$ (1) Å, $b = 11.72$ (2) Å, $c = 20.22$ (8) Å, $\alpha = \beta = \gamma = 90°$. The Ni appears to be at crystallographic centers of symmetry for both forms, thus ruling out tetrahedral configurations. The position of the Ni makes further X-ray studies extremely difficult.

TABLE II

LIGAND FIELD SPECTRA[a]

R	Medium	$\tilde{\nu}_{max}$, cm^{-1} (ϵ_M)		
H	$CHCl_3$	19,700 (68)[b]	22,800 (100)	
CH_3	$CHCl_3$	19,200 (200)		
Brown	Nujol	18,200[b]	21,900	
Blue	Nujol	17,100		~8300[c]
i-C_3H_7	$CHCl_3$	19,100 (190)		
sec-C_4H_9	$CHCl_3$	18,800 (230)		
C_6H_5	$CHCl_3$	18,700 (80)[b]	20,700 (112)	
o-$C_6H_4CH_3$	$CHCl_3$	18,000 (94)	20,500 (144)	
p-$C_6H_4CH_3$	$CHCl_3$	18,100 (106)	20,600 (164)	
$C_6H_5CHCH_3$	$CHCl_3$	18,900 (224)		

[a] All data obtained at room temperature. [b] Shoulder. [c] Weak, broad band.

TABLE III

MAGNETIC MOMENTS FOR SOLIDS AND SOLUTIONS

R	Solid μ_{eff}, BM[a,b]	Solutions[c]				
		Concn, M	Temp, °C	μ_{eff}, BM[b,d]	% tetrahedral[e]	$\Delta G°$, kcal/mol
H	<0.5					
CH_3 (brown)	1.0					
CH_3 (blue)	3.2[f]					
i-C_3H_7	1.0	0.04	40	1.1	11	1310
			50	1.15	12	1270
			65	1.3	15	1180
sec-C_4H_9	0.5	0.18	31	0.9	8	1470
			39	1.0	9	1400
			50	1.1	12	1280
			60	1.2	13	1250
C_6H_5	<0.5					
o-$C_6H_4CH_3$	<0.5					
p-$C_6H_4CH_3$	<0.5					
$C_6H_5CHCH_3$	1.4	0.10[g]	27	0.85	7	1580
			38	0.85	7	1640
			49	1.0	9	1510
			63	1.1	12	1360

[a] By the Gouy method. [b] Corrected for ligand diamagnetism. [c] Solvent mixture: 90% dried $CHCl_3$–10% TMS (v/v). [d] By Evans' method. [e] Per cent tetrahedral = $100(\mu_{eff}/\mu_t)^2$, where μ_t = 3.3 BM.[2] [f] Estimated error of ±0.1 BM. [g] Assumed 20% ligand impurity.

Magnetic Susceptibilities.—Table III lists the μ_{eff} values for solid samples calculated with the equation

$$\mu_{eff} = 2.84\sqrt{\chi_M T} \qquad (1)$$

where χ_M is the molar susceptibility corrected for ligand diamagnetism using Pascal's constants.[15] For all of the complexes, except the blue form of the R = CH_3 compound, the low values of the magnetic moments are indicative of a substantial fraction of planar form. The blue species has a μ_{eff} of 3.1 ± 0.1 BM which is in the range of magnetic moments reported for certain polymerized quasioctahedral salicylaldimine complexes (B) in the solid state[2] and supports the proposal that the blue substance is a polymer of a planar, brown form.

The magnetic susceptibilities of chloroform solutions were determined by the Evans method. The standard equation[2]

$$\chi_g = \frac{3\Delta f}{2\pi f m} + \chi_0 + \frac{\chi_0(d_0 - d_s)}{m} \qquad (2)$$

was used where χ_g and χ_0 are the gram-susceptibilities of the solute and solvent, respectively; Δf is the frequency separation of the two tetramethylsilane signals; f is the frequency of the spectrometer, 60 × 10^6 Hz; m is the mass of solute per milliliter of solution; and d_0 and d_s are the densities of the solvent and solution, respectively. The value of χ_0 was calculated from the gram-susceptibilities of the pure chloroform and TMS, weighted by the weight fractions in the solvent mixture. A value of -0.49×10^{-6} cgsu was taken as the gram-susceptibility of the alcohol-free chloroform,[19] and the value of the gram-susceptibility of TMS was approximated using Pascal's constants.[15] The ratio $(d_0 - d_s)/m$ was positive, being about 0.1, and decreased with temperature. The magnetic moments were calculated from the molar susceptibilities using eq 1. Owing to solubility limitations, the values of Δf were less than 10 Hz and for R = i-C_3H_7 were less than 3 Hz. Furthermore some clouding of the solutions was noted. For R = $C_6H_5CHCH_3$ the nmr spectrum showed about 20% ligand impurity which was corrected for in the calculations of the molar susceptibility.

Values of $\Delta G°$ given in Table III were calculated from the equation

$$\Delta G° = RT \ln K_{eq} = RT \ln \left[(\mu_t/\mu_{eff})^2 - 1\right] \qquad (3)$$

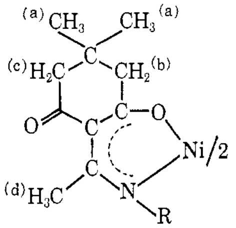
where K_{eq} is the equilibrium constant for the planar–tetrahedral interconversion and μ_t = 3.3 ± 0.1 BM is the magnetic moment for the fully tetrahedral species.[2] The resulting $\Delta G°$ values are presented in Table III and for R = sec-C_4H_9 are plotted in Figure 1.

---

(19) G. Foex, "Constantes Selectionees Diamagnetism and Paramagnetism," Masson and Cie, Paris, 1957.

TABLE IV

CHEMICAL SHIFT DATA[a]



R		a	b	c	d	Resonances
H	Ligand	1.04	2.38	2.38	2.56	7.40 (H)
	Complex	0.97	2.23	2.23	2.45	5.65 (H)
CH_3	Ligand	1.04	2.36	2.36	2.58	3.09 doublet (CH_3)
	Complex	0.98	2.16	2.26	2.21	2.81 (CH_3)
i-C_3H_7	Ligand	1.02	2.34	2.34	2.54	1.30 doublet (CH_3) 3.90 multiplet (H)
	Complex	1.10	−2.30	2.24	1.30	5.65 doublet (CH_3) (H not detected)
sec-C_4H_9	Ligand	1.04	2.36	2.36	2.57	1.28 doublet (α-CH_3) 0.97 triplet (β-CH_3) 1.62 multiplet (CH_2) 3.70 sextet (CH)
	Complex (racemic)	0.97	−1.03 −1.38	2.25	1.38 1.48	3.95 (α-CH_3) 4.46 2.50 (β-CH_3) 5.65 (CH_2) (CH not detected)
	Complex (active)	0.92	−0.93	2.25	1.48	3.89 (α-CH_3) 2.46 (β-CH_3) 5.50 (CH_2) (CH not detected)
C_6H_5	Ligand	1.07	2.41	2.41	2.50	~7.2 (C_6H_5)
	Complex	0.79	1.33	2.13	1.94	7.22 (C_6H_5)
o-$C_6H_4CH_3$	Ligand	1.08	2.45	2.45	2.25	7.25 (C_6H_4) 2.50 (CH_3)
	Complex	0.78	1.30	2.12	1.88	7.08 (C_6H_4) 2.59 (CH_3)
p-$C_6H_4CH_3$	Ligand	1.10	2.44	2.44	2.40	7.17 (C_6H_4) 2.51 (CH_3)
	Complex	0.80	1.36	2.17	1.97	7.10 (C_6H_4) 2.34 (CH_3)
$C_6H_5CHCH_3$	Ligand	1.05	2.42	2.42	2.50	7.31 (C_6H_5) 1.64 doublet (CH_3) 4.88 quartet (CH)
	Complex	0.99	−2.79[b]	2.14	1.55 1.65	7.24 (C_6H_5) 7.24 (CH_3) (CH not detected)

[a] Chemical shifts of $CDCl_3$ solutions measured in ppm from an internal standard, tetramethylsilane. Negative values indicate resonances at higher field than the standard. [b] Center of AB quartet, chemical shift difference 0.78 ppm, $J = 18$ Hz.

As anticipated for a planar–tetrahedral equilibrium, the per cent of tetrahedral species increases with temperature. Within experimental error it is estimated that solutions of the three complexes where R = i-C_3H_7, *sec*-C_4H_9, and $C_6H_5CHCH_3$ contain 5–10% of the tetrahedral form at 30°, the percentage increasing in the order $C_6H_5CHCH_3$ < *sec*-C_4H_9 < i-C_3H_7. Solutions of the other five bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes are diamagnetic over a temperature range of 30–60° and thus contain an immeasurable amount of tetrahedral species at these temperatures.

Proton Magnetic Resonances.—The pmr data recorded at room temperature (about 30°) for the eight complexes and corresponding ligands are compiled in Table IV. Except for the three complexes where R = i-C_3H_7, *sec*-C_4H_9, and $C_6H_5CHCH_3$, the resonances appear as sharp bands indicative of diamagnetic species and hence a planar configuration. The chemical shifts are independent of temperature over a 30–60° range and are independent of concentration between 50 and 100 m*m*. Even at temperatures as low as −5°, the R = o-$C_6H_4CH_3$ and p-$C_6H_4CH_3$ derivatives showed no temperature-dependent chemical shifts. The lack of dependence on temperature and concentration indicates that the planar complexes exhibit no planar–tetrahedral or planar–octahedral equilibria under the experimental conditions used.

There is only a slight shift of the ligand resonances upfield upon formation of the planar complexes. Ex-

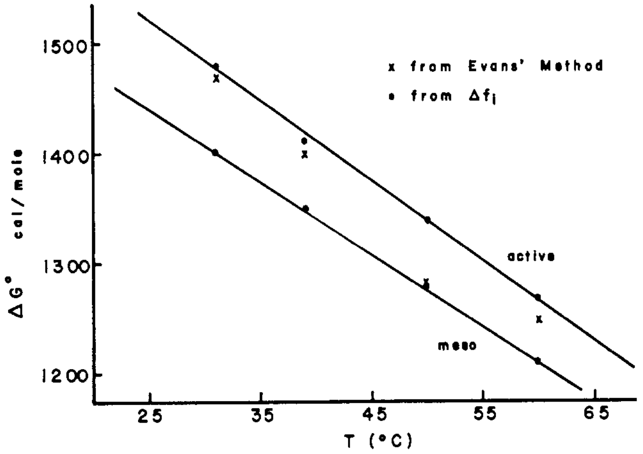


Figure 1.—Temperature dependence of the free energy change for the planar–tetrahedral conversion of bis(N-*sec*-butyl-2-acetiminodimedonato)nickel(II).

cept for the case of R = H, the complexation removes the equivalence of the 4-methylene (c) and 6-methylene (b) resonances, the 6-methylene peak appearing at higher field. The shift of the 6-methylene protons is particularly noticeable for the R = aryl compounds and may be due to a ring-current effect of the phenyl group of the neighboring ligand. In the *trans* isomer, which is usually the more stable isomer,[20] the 6-methylene group is in close proximity of the N substituent. Evidently a $C_6H_5CHCH_3$ group on the nitrogen is sufficiently bulky to render the two 6-methylene protons nonequivalent as indicated by an AB quartet for the 6-methylene group resonance. The analysis of the multiplet as an AB quartet was confirmed by recording the spectrum at 100 MHz as well as at 60 MHz.

Table V

Contact Shifts, Coupling Constants, and Thermodynamic Parameters (300°K)

R	Position	Δf_i, Hz[a]	a_i, G	$\Delta G°$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, eu
i-C_3H_7	(b)	286	−0.45	1.40	3.3	6.2
	(d)	75	−0.14			
sec-C_4H_9	(b) *meso*	232	−0.38	1.43	3.5	6.8
	active	211		1.50		
	(d) *meso*	71	−0.12			
	active	65				
$C_6H_5CHCH_3$	(b)	320	−0.65	1.55	2.1	1.8
	(d)	98	−0.20			

[a] Δf_i values were measured relative to the free ligand in the same solvent and were calculated from the relationship $\Delta f_i = \Delta f_i(\text{complex}) - \Delta f_i(\text{ligand})$.

The chemical shifts of the three complexes containing α-branched alkyl nitrogen substituents, R = *i*-C_3H_7, *sec*-C_4H_9, and $C_6H_5CHCH_3$, do vary with temperature but not with concentration. The temperature dependence of the spectra is interpreted in terms of proton resonance contact shifts resulting from a planar–tetrahedral equilibrium. Assuming that the transfer of spin density in these complexes is similar to the behavior of β-ketoamine complexes with the spin imbalance in the lowest filled π molecular orbital of the odd-alternant ligand system,[8] the signals of the 6-methylene (b) and the acetyl (d) proton are expected to shift upfield from the corresponding free-ligand resonances while the peaks of any nitrogen substituent are expected to shift downfield, the shifts increasing with an increase in temperature. Such changes in chemical shifts are observed. The contact shifts are largest for the 6-methylene (b) and acetyl (d) resonances, and these values are listed in Table V.

Two signals are observed for the 6-methylene resonance and for the acetyl resonance of the complex where R = *sec*-C_4H_9. When the complex is prepared from optically pure *sec*-butylamine, the higher field signal in each pair disappears (see Figure 2). Hence the doubling of signals is due to the active and *meso* isomers of the complex. This distinction between diastereoisomers has been observed for other nickel(II) complexes containing asymmetric centers and has been attributed to the difference in free energy changes ($\Delta G°_{\text{active}} \neq \Delta G°_{meso}$) of the planar–tetrahedral conversion for the two forms.[9,21] The difference arises in the paramagnetic or tetrahedral configuration.[22] The absence of any observable distinction between the pmr spectra of the active and *meso* diastereoisomers of the complex with R = $C_6H_5CHCH_3$ is presumably a consequence of the very small per cent of tetrahedral species. Alternatively the resolved ligand might have racemized almost completely in the synthesis of the nickel(II) complex. This, however, seems less likely since the specific rotation recorded for the optically active complex in chloroform solution is $[\alpha]^{25}_{578}$ −520° whereas we have $[\alpha]^{25}_{578}$ −580° for the R = (+)-*sec*-C_4H_9 complex.

The relationship between the proton contact shifts and the free energy change for the planar–tetrahedral conversion is given by the equation[6]

$$\Delta f_i/f = -a_i(\gamma_e/\gamma_H)\frac{g\beta S(S+1)}{6SkT}[1 + \exp(\Delta G°/RT)]^{-1} \quad (4)$$

where a_i is the coupling constant between the unpaired spin at the ith carbon and the magnetic moment of the

---

(20) E. Frasson, C. Panatonni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959).

(21) M. J. O'Connor, R. E. Ernst, and R. H. Holm, *J. Am. Chem. Soc.*, **90**, 4561 (1968).

(22) R. H. Holm, A. Chakravorty, and G. O. Dudek, *ibid.*, **86**, 379 (1964).

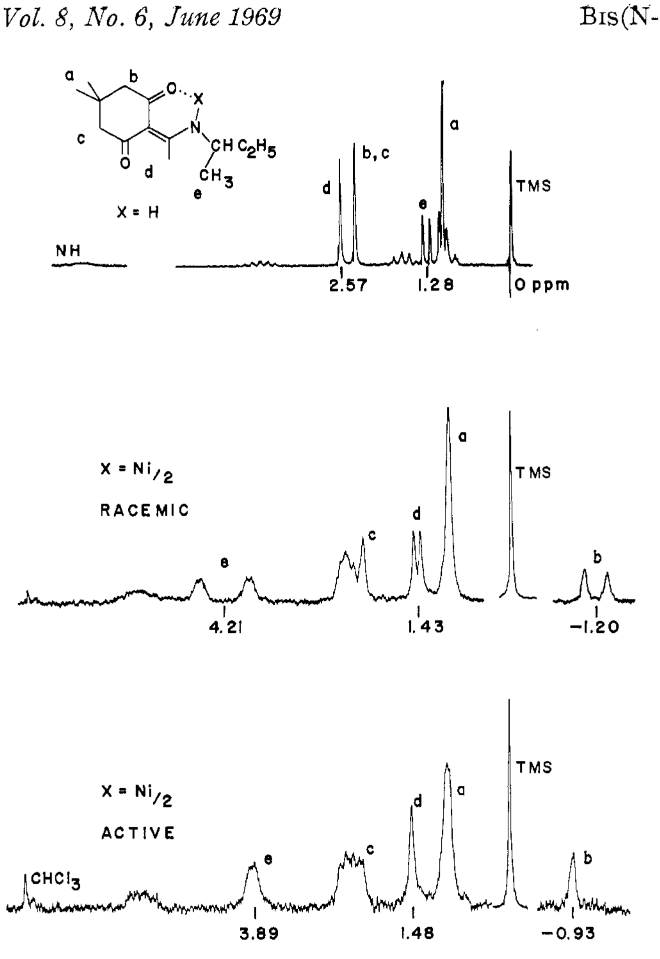


Figure 2.—Proton magnetic resonance spectra of bis(N-*sec*-butyl-2-acetiminodimedonato)nickel(II) in $CDCl_3$ solution at 30°.

proton, g is the g value of the paramagnetic form and is equal to $\mu_t/\sqrt{2}$, γ_e and γ_H are the magnetogyric ratios of the electron and proton, respectively, β is the Bohr magneton, and S is the total electron spin ($S = 0$, planar; $S = 1$, tetrahedral). Equation 4 has been used to calculate values of a_i from Δf_i and from those values of $\Delta G°$ which were calculated through eq 3 and listed in Table III. Since a_i is expected to be independent of temperature and since no systematic variation with temperature was observed, average values of a_i are presented in Table V.

The principal source of error in the calculation of a_i quantities lies in the uncertainty of the μ_{eff} values determined by the Evans method. By averaging the a_i values some of the error may be compensated. Using the average a_i values and eq 4, new values of $\Delta G°$ have been obtained and are given in Table V and are presented in Figure 1 for R = *sec*-C_4H_9. These values of $\Delta G°$ may well be more reliable for they are computed from contact shifts of more than 200 Hz whereas the chemical shifts measured in Evans' procedure were less than 10 Hz. The discrepancy between the $\Delta G°$ values obtained by the two approaches is greatest for R = $C_6H_5CHCH_3$ for which the observed decomposition was most pronounced. The percentages of tetrahedral form at 300°K calculated from the $\Delta G°$ quantities in Table V and eq 3 are: 8.7, R = *i*-C_3H_7; 7.8, R = *sec*-C_4H_9 (*meso*); 7.5, R = *sec*-C_4H_9 (active); 6.9, R = $C_6H_5CHCH_3$. Within the errors of the experimental measurements, it may be concluded that the proportion of tetrahedral form for any of the bis(N-substituted 2-acetiminodimedonato)nickel(II) complexes investigated is less than 10% and the amount of tetrahedral species increases in the order $C_6H_5CHCH_3$ < *sec*-C_4H_9 < *i*-C_3H_7.

Over the small temperature range considered, 30–60°, the variation of $\Delta G°$ is nearly linear with temperature (*cf.* Figure 1). Thus from a plot of $\Delta G°$ *vs.* temperature and the equation $\Delta G° = \Delta H° - T\Delta S°$, values of $\Delta H°$ and $\Delta S°$ have been computed and are tabulated in Table V. Within the accuracy of the calculations, $\Delta S°$ is the same for the *meso* and the active R = *sec*-C_4H_9 diastereoisomers.

Of the three complexes exhibiting a planar–tetrahedral equilibrium in solution, the one with the smallest tetrahedral percentage, namely, R = $C_6H_5CHCH_3$, displays a significantly lower $\Delta S°$ and lower $\Delta H°$ values. This indicates that the equilibrium is governed primarily by an entropy rather than an enthalpy factor. According to previously presented arguments,[8,23] the magnitude of $\Delta S°$ may be determined primarily by solvent effects. Owing to steric shielding by the α-branched alkyl substituent on nitrogen, hydrogen bonding of the type O···D–CCl_3 with the coordinating oxygen in the tetrahedral form may be considerably less than in the planar form. The R = C_6H_5CH-CH_3 group, however, which is sufficiently bulky to render nonequivalent the two 6-methylene protons, may hinder the solute–solvent interaction in the planar form to produce only a small entropy change for the planar–tetrahedral conversion.

Conclusions

The bis(N-substituted 2-acetiminodimedonato)-nickel(II) (C) compounds display none of the intermolecular association observed for R = aryl derivatives of the β-ketoamine (A) and salicylaldimine (B) complexes and for R = CH_3 and $C_6H_5CHCH_3$ derivatives of salicylaldimine (B) complexes. The low magnetic moments of solid samples of the C-type complexes indicate that all of these compounds are predominantly planar in the solid state in contrast to the A and B derivatives with R = α-branched alkyl which are generally tetrahedral solids with $\mu_{eff} \approx 3.3$ BM.[1] In chloroform solutions of the C complexes only the three R = α-branched alkyl compounds give evidence of a planar–tetrahedral equilibrium according to magnetic susceptibility and proton magnetic resonance measurements. At room temperature the amount of the tetrahedral form in chloroform solution is less than 10% increasing in the order $C_6H_5CHCH_3$ < *sec*-C_4H_9 < *i*-C_3H_7. This is the same relative order but at a considerably lower per cent of the tetrahedral form than reported for analogous nickel(II) complexes of β-ketoamine (A) or salicylaldimine (B) derivatives. For β-ketoamines, the analogous derivatives are primarily tetrahedral,[8] and for salicylaldimines, the R = $C_6H_5CHCH_3$ compound is 15% tetrahedral while the R = *sec*-C_4H_9 and *i*-C_3H_7 compounds are about 50% tetrahedral under the same experimental conditions.[2,3] It can be concluded that the nonaromatic dimedone ring promotes a planar configuration of bidentate Schiff base complexes of nickel(II) to a significantly greater extent than does either the open chain of the β-ketoamines or the aromatic ring of the salicylaldimines. Also the dimedone ring inhibits intermolecular association to a greater degree than do the other two ligand "backbones."

Acknowledgment.—We thank Dr. Gerald O. Dudek for helpful suggestions. We are indebted to Harvard University for the use of various instruments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

CONTRIBUTION FROM THE MCPHERSON AND EVANS CHEMICAL LABORATORIES,
THE OHIO STATE UNIVERSITY, COLUMBUS, OHIO 43210

Stereospecific Formation of Chelate Sandwich Compounds Derived from *o*-Aminobenzaldehyde and 2-Amino-5-chlorobenzaldehyde by a Metal Ion Induced Rearrangement

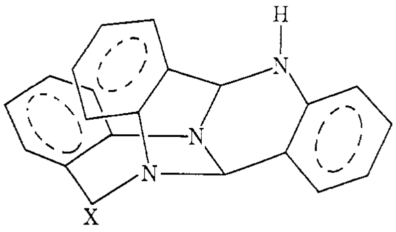
BY LARRY T. TAYLOR[1] AND DARYLE H. BUSCH

Received November 11, 1968

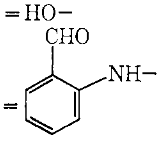
13-Hydroxy-6,12-benzo-6H-quinazolino[3,4-*a*]quinazoline $(oab)_3$ rearranges under the influence of nickel(II) ion to produce the known closed tridentate macrocyclic ligand tribenzo[*b,f,j*][1,5,9]triazacycloduodecine (TRI). This metal ion induced rearrangement has been used to synthesize a complex containing two trimeric condensates bound to each nickel(II) ion, $Ni(TRI)_2^{2+}$. The resultant complexes exhibit octahedral stereochemistry with the three donor nitrogen atoms of each macrocycle occupying a face of the octahedron. Two geometrical arrangements are possible for these complexes depending upon the clockwise or counterclockwise progression of the repeating unit (as viewed down the major threefold axis of rotation) in each macrocyclic Schiff base moiety. Reactions with partially resolved $Ni(TRI)(H_2O)_3^{2+}$ indicate that $Ni(TRI)_2^{2+}$ exists in the *meso* form exclusively.

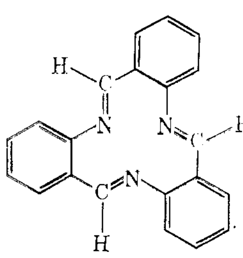
Introduction

The metal ion controlled stereochemical course of a chemical reaction is dramatically demonstrated in the self-condensation of *o*-aminobenzaldehyde. A bis anhydro trimer, $(oab)_3$ (Ia), and tris anhydro tetramer (Ib) are produced in the absence of metal ions;[2] whereas in the presence of nickel(II) ion, two complexes containing closed tridentate[3] (TRI) and tetradentate[4] (TAAB) macrocyclic ligands, respectively, are isolated. The tridentate ligand is shown as II. A complex possessing solely the tetradentate macrocyclic ligand is prepared in the presence of copper(II).[4] The structures of the ligands in these complexes have been established by X-ray studies.[5]



Ia, X— = HO—

Ib, X— =




II

In a previous communication we reported preliminary results[6] concerning the role of the metal ion in these self-condensation reactions in addition to the preparation of a novel chelate sandwich compound. We wish now to report these findings in more detail as well as to describe a unique stereospecific reaction involving these materials.

Experimental Section

Materials.—*o*-Aminobenzaldehyde and 2-amino-5-chlorobenzaldehyde were prepared by the method of Smith and Opie[7] using 2-nitrobenzaldehyde and 5-chloro-2-nitrobenzaldehyde as precursors. The method described by McGeachin[2] was employed

---

[1] National Institutes of Health postdoctoral fellow, 5-F2-GM-28, 091-03.

[2] S. G. McGeachin, *Can. J. Chem.*, **44**, 2323 (1966).

[3] G. A. Melson and D. H. Busch, *J. Am. Chem. Soc.*, **87**, 1706 (1965).

[4] G. A. Melson and D. H. Busch, *ibid.*, **86**, 4834 (1964).

[5] E. B. Fleischer and E. Klem, *Inorg. Chem.*, **4**, 637 (1965); S. W. Hawkinson and E. B. Fleischer, private communication, 1968.

[6] L. T. Taylor, S. C. Vergez, and D. H. Busch, *J. Am. Chem. Soc.*, **88**, 3170 (1966).

[7] L. I. Smith and J. W. Opie, *Org. Syn.*, **28**, 11 (1948).