bis (which results in the case of the other tin(II) halides[4]) may be due to the insolubility of SnF_2 in tetrahydrofuran, so that $Co_2(CO)_8$ is always in large excess, and the $F_2Sn[Co(CO)_4]_2$ which presumably forms in an initial insertion reaction will react further to produce $FSn[Co(CO)_4]_3$.

The product occurs as dark red needles which are moderately air stable. It is moderately soluble in *n*-pentane and readily soluble in polar solvents, differing very strikingly in this respect from organotin fluorides, which as a rule are very low in solubility in organic solvents.[16] The ^{19}F nmr shows a singlet at 122.9 ppm in chloroform and at 117.7 ppm in C_6H_6, both values relative to $CFCl_3$. No peaks due to tin–fluorine spin–spin coupling were observed within 1500 cps of the main peak.

Tin(II) Acetate Derivatives.—Reaction of tin(II) acetate with cobalt carbonyl in tetrahydrofuran solution afforded a fairly low yield of a mixture of orange needles and dark red crystals. These were characterized by analysis as $(CH_3CO_2)_2Sn[Co(CO)_4]_2$ and $CH_3CO_2Sn[Co(CO)_4]_3$. The mass spectrum of the diacetate has no fragments higher than *m/e* 524, which can be assigned to either $(CH_3CO_2)_2SnCo_2(CO)_6^+$ or $(CH_3O)_2SnCo_2(CO)_8^+$; fragments due to consecutive loss of CO from this were also observed, as well as $SnCH_3CO_2^+$ and $Sn(CH_3CO_2)_2^+$.

The molecular weight of the diacetate in cyclohexane indicated a considerable degree of association: observed values were in the 750–800 range, with 578 the calculated value for $(CH_3CO_2)_2Sn[Co(CO)_4]_2$. Such association is well known in organotin carboxylates,[17] and might account for the somewhat different carbonyl stretching pattern compared with that usually observed for bis(tetracarbonylcobalt) derivatives.[2,4] The pattern of carbonyl stretching bands for $CH_3CO_2Sn[Co(CO)_4]_3$ is somewhat different from that of $ClSn[Co(CO)_4]_3$, in that the two very strong bands observed in the latter[3] both possess strong shoulders in the former. This may possibly be due to a reduction in symmetry from C_{3v} to C_s by the asymmetric nature of the acetate group.

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CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY,
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Comparative Stereochemical Populations and Thermodynamics of Structural Interconversion of Planar and Tetrahedral Cobalt(II) and Nickel(II) Complexes

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A series of new bis(β-ketoamino)cobalt(II) and -nickel(II) complexes of general formulation $M(R-R_\gamma R_\beta R_\alpha)_2$ have been prepared in which R is the donor nitrogen substituent and R_γ, R_β, R_α are the chelate ring carbon atom substituents. It has been demonstrated from spectral, magnetic, and nmr measurements that cobalt complexes with $R = H$ and nickel complexes with $R = CH_3$ undergo the planar $\rightleftharpoons$ tetrahedral configurational equilibrium in chloroform solution and that cobalt ($R = CH_3$) and nickel ($R = H$) complexes exist exclusively in solution as the tetrahedral and planar stereoisomers, respectively. A series of equilibrium pairs comprised of $Ni(CH_3-R_\gamma R_\beta R_\alpha)_2$ and $Co(H-R_\gamma R_\beta R_\alpha)_2$ complexes, which possess the minimal ligand structural differences possible for direct measurement and comparison of the configurational equilibria, were examined in chloroform solution. Thermodynamic quantities characterizing the configurational changes were obtained from measurement of the temperature dependence of the contact shifts (nickel) and magnetic susceptibilities (cobalt). Stereochemical populations for the pairs were found usually to parallel one another. The relative equilibrium positions of the members of each pair are controlled principally by enthalpy effects. The stability differences between tetrahedral and planar Ni(II) ($R = CH_3$) were found to be $\sim$2–4 kcal/mole greater than those between tetrahedral and planar Co(II) ($R = H$). These differences were concluded to arise mainly from differences in the crystal field stabilization energies and metal–ligand bond energies of Ni(II) and Co(II) in their two stereoisomeric configurations. Stability differences corrected for CFSE effects could not be obtained because of the lack of information required to estimate CFSE values for the planar configurations of each metal.

Introduction

In formulating the structural systematics of complexes of the divalent transition metal ions having their most common coordination numbers as six and four, there are two problems of special general significance. The first of these involves determination of the relative stabilities of six- and four-coordinate complexes as the metal ion is varied in the sequence Mn(II)–Zn(II). Solution investigations are the most feasible and the existing data from equilibrium and thermodynamic studies[3,4] indicate that the actual

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stability of the four-coordinate relative to the six-coordinate configuration varies irregularly in this sequence and maximizes at Zn(II). The irregularities in relative stabilities have been interpreted in terms of crystal field stabilization energy (CFSE) effects.

The second problem concerns the relative stabilities of stereoisomers of the same coordination number. For four-coordinate complexes the idealized limiting stereochemistries are planar and tetrahedral, and a quantitative examination of the relative stabilities of these two configurations as a function of ligand structure and coordinated metal is possible if an equilibrium between them can be achieved. We are currently investigating the occurrence of such an equilibrium or the predominant stereochemistry in noncoordinating solvents for bis-chelate complexes of Cr(II)–Zn(II).[5] In this report attention is directed to a comparison of the configurational equilibria of Co(II) and Ni(II) complexes.

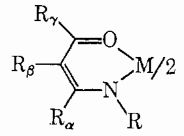
It has been recognized for some time that the stereochemistry of four-coordinate Co(II) is predominantly tetrahedral; in fact, more tetrahedral complexes have been established for divalent cobalt than for any other transition metal ion.[6] In contrast, the four-coordinate complexes of Ni(II) far more often assume a planar stereochemistry. For complexes with identical ligands which are not constrained by the ligand to be either tetrahedral or planar and, therefore, presumably are able to assume the lowest energy structure, the usual stereochemical pattern is Ni(II)—planar and Co(II)—tetrahedral, in both solid and solution phases. Clear-cut examples of this pattern are furnished by bis(dipivaloylmethanato)nickel(II)[7] and -cobalt(II),[8] bis(O,O′-diethyldithiophosphato)nickel(II)[9] and -cobalt(II),[10] and bis(1-pyrazolyl)boratonickel(II) and -cobalt(II).[11]

The fundamental structural equilibria for four-coordinate Ni(II) and Co(II) complexes in noncoordinating solvents are (1) and (2), respectively.

$$\text{planar } (S = 0) \rightleftharpoons \text{tetrahedral } (S = 1) \qquad (1)$$

$$\text{planar } (S = {}^1/_2) \rightleftharpoons \text{tetrahedral } (S = {}^3/_2) \qquad (2)$$

Equilibrium 1 is well established for an extensive series of bis-chelate complexes[12–15] including those of α,β-unsaturated β-ketoamines, **1**, M = Ni.[13f,15] The available thermodynamic parameters for the structural change reveal that the planar configuration is inherently more stable for Ni(II) in the absence of severe steric interactions such as can be imposed by bulky nitrogen substituents. Various types of solution equilibria involving ostensibly four-coordinate Co(II) complexes have been established, but most of these implicate species with an effective coordination number exceeding four.[16,17] Equilibrium 2 has thus far been demonstrated only for a series of β-ketoamine complexes, **1**, M = Co, R = H.[16]



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The existence of equilibria 1 and 2 for complexes with the same general ligand structure (β-ketoamine) provides a previously unavailable opportunity for the semiquantitative assessment of the relative stabilities of planar *vs.* tetrahedral Co(II) compared to Ni(II) in these configurations. Herein is presented a comparison of thermodynamics of the configurational change for Ni(II) and Co(II) complexes of structure 1 as measured from the temperature dependence of proton contact shifts (nickel) and magnetic susceptibilities (cobalt). The various enthalpy and entropy factors contributing to the markedly different equilibrium positions of (1) and (2) are considered in more detail than before.

Experimental Section

Preparation of Ligands.—The α,β-unsaturated β-ketoamines used in this investigation were prepared as previously described by reaction of the appropriate β-diketone and primary amine.[15,16] They were identified by their pmr spectra and were not further characterized.

Pivaloylacetone was prepared by the method of Adams and Hauser;[18] 2-naphthoylacetone was obtained following the procedure of Banchetti.[19] Benzoylacetaldehyde was synthesized according to Bülow and von Sicherer.[20]

Preparation of Complexes.—Certain of the complexes utilized in this study have already been reported.[16] The new bis(β-ketoamino)cobalt(II) and -nickel(II) complexes were prepared by the nonaqueous chelation procedure described previously.[15,16] Characterization data for 13 new complexes are given in Table I. Bis(1-phenyl-3-methylamino-2-propen-1-ono)nickel(II) was first prepared by Jäger,[21] who gave an incomplete analysis and a melting point of 200°; this complex has been more fully characterized in this work. Bis(2,2-dimethyl-5-isopropylamino-4-hexen-3-ono)nickel(II) was not obtained analytically pure despite numerous attempts at purification; the contaminant apparently was free ligand.

By the usual procedure[15,16] bis(1,1,1-trifluoro-4-amino-3-pen-

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TABLE I

CHARACTERIZATION OF BIS(β-KETOAMINO)METAL(II) COMPLEXES

R_γ	R_β	R_α	R	M	Solvent[a]	Mp,[b] °C	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
CH_3	CH_3	H	CH_3	Ni[c]	H	108–110	50.93	51.22	7.12	7.25	9.90	9.77
$C(CH_3)_3$	H	CH_3	H	Ni[d]	H	190–191	56.67	56.38	8.32	8.50	8.26	8.33
$C(CH_3)_3$	H	CH_3	H	Co[e]	H	128–129	56.63	56.41	8.32	8.31	8.26	8.45
$C(CH_3)_3$	H	CH_3	CH_3	Ni[f]	H	151–152	58.88	58.76	8.79	8.52	7.63	7.64
$C(CH_3)_3$	H	CH_3	$i\text{-}C_3H_7$	Ni[g,k]	H	124–127	62.42	61.34	9.53	9.30	6.62	5.89
CF_3	H	CH_3	CH_3	Ni[h,l]	H	128–129	36.86	37.09	3.61	3.74	7.17	7.28
CF_3	H	CH_3	CH_3	Co[e]	H	200–201	36.84	37.38	3.61	3.88	7.16	7.05
CF_3	H	CH_3	$i\text{-}C_3H_7$	Ni[i,m]	H	145–146	42.98	42.90	4.96	5.06	6.27	6.47
C_6H_5	H	H	CH_3	Ni[c,n]	T–H	198–199	63.36	62.81	5.32	5.13	7.39	7.30
C_6H_5	H	H	$i\text{-}C_3H_7$	Ni[c]	H	166–168	66.23	66.07	6.49	6.45	6.44	6.50
$\beta\text{-}C_{10}H_7$	H	CH_3	H	Co[e]	T	217–218	70.14	70.36	5.05	5.03	5.84	5.99
$\beta\text{-}C_{10}H_7$	H	CH_3	CH_3	Ni[c]	T	244–245	71.03	71.24	5.56	5.59	5.52	5.31
$\beta\text{-}C_{10}H_7$	H	CH_3	CH_3	Co[d]	T	280 dec	71.00	70.44	5.56	5.69	5.52	5.65
$\beta\text{-}C_{10}H_7$	H	CH_3	$i\text{-}C_3H_7$	Ni[j]	H	232–234	72.48	72.64	6.44	6.33	4.97	5.20

[a] Solvent used for extraction and recrystallization: H, *n*-heptane; T, toluene; T–H, 1:1 mixture. [b] Uncorrected. [c] Green. [d] Red. [e] Orange. [f] Red-brown. [g] Brown. [h] Gray. [i] Green-brown. [j] Gold. [k] Contaminated with uncomplexed ligand. [l] F: calcd, 29.16; found, 29.38. [m] F: calcd, 25.50; found, 25.77. [n] Previously reported.[21]

TABLE II

MAGNETIC MOMENTS IN SOLID AND SOLUTION PHASES[a]

Complex	Solid μ_{eff}, BM	Solution Solvent	Solution μ_{eff}, BM
$Ni(i\text{-}C_3H_7\text{–}CF_3HCH_3)_2$	3.26[b]	$CHCl_3$	3.31[b]
$Ni(i\text{-}C_3H_7\text{–}C_6H_5HH)_2$	Brown form: 2.95[c]	$CHCl_3$	3.05[b]
	Green form: diamagnetic		
$Ni(i\text{-}C_3H_7\text{–}NapHCH_3)_2$	3.20[b]	$CHCl_3$	3.24[b]
$Ni(i\text{-}C_3H_7\text{–}t\text{-}C_4H_9HCH_3)_2$	. . .	$CHCl_3$–TMS[d]	3.08[b,e]
$Co(H\text{–}t\text{-}C_4H_9HCH_3)_2$	2.36[b]	$CHCl_3$	2.80[b]
		$CHCl_3$–TMS[d]	2.94[b]
		$CHCl_3$–TMS[d]	3.78[f] (33°)
$Co(H\text{–}NapHCH_3)_2$	2.08[b]	. . .[g]	
$Co(CH_3\text{–}NapHCH_3)_2$	4.28[c]	$CHCl_3$	4.26[b]
$Co(H\text{–}CF_3HCH_3)_2$	2.17[c]	$CHCl_3$–TMS[d]	3.78[c] (33°)
		$CHCl_3$–TMS[d]	3.67[b]
$Co(CH_3\text{–}CF_3HCH_3)_2$	4.26[c]	$CHCl_3$–TMS[d]	4.36[f] (46°)

[a] All values obtained at ambient room temperature (20–26°) unless otherwise indicated. [b] Gouy method. [c] Faraday method. [d] 15% v/v tetramethylsilane in chloroform. [e] Impure sample. [f] Nmr method. [g] Insufficiently soluble for accurate measurement.

ten-2-ono)cobalt(II) and its 4-methylamino analog could be obtained in low yields only. The crude reaction product in both cases consisted of a small amount of red, crystalline material in addition to a larger quantity of orange or yellow material. Samples of the red crystals gave unsatisfactory elemental analyses and unexpectedly large gram-susceptibilities. The yellow or orange products were separated from the red material by repeated fractional crystallization from *n*-heptane and gave satisfactory elemental analyses for the bis-chelate formulation.

Magnetic Susceptibility Measurements.—Determinations by the Gouy and nmr[22] methods were carried out as before.[15,16] Susceptibilities of solids prepared in small quantities were obtained by the Faraday method on an apparatus consisting of a Cahn gram electrobalance adapted for use with an Alfa 4-in. electromagnet equipped with Heyding pole caps. The calibrant was $HgCo(NCS)_4$.[23] Susceptibilities were corrected for diamagnetism, and magnetic moments were calculated from the Curie law: $\mu_{eff} = 2.83(\chi^{M}_{cor}T)^{1/2}$. Data are given in Table II.

Proton Resonance Measurements.—Pmr spectra were recorded at ambient temperature or over a temperature range by use of a Varian HR-60, HA-100, or A-60A instrument. Tetramethylsilane was used as the internal reference in all cases. Chemical shifts were measured by the usual side-band technique, and contact shifts and coupling constants for the Ni(II) complexes were determined by a procedure described previously.[15] The coupling constants given for bis(2,2-dimethyl-5-isopropylamino-4-hexen-3-ono)nickel(II) were calculated assuming no ligand exchange and an exclusively tetrahedral structure with μ_{eff} = 3.35 BM. Previously unpublished contact shifts and coupling constants are given in Table III.

TABLE III

CONTACT SHIFTS AND COUPLING CONSTANTS OF PSEUDO-TETRAHEDRAL NICKEL(II) COMPLEXES

Complex	Position	Δf_i,[a] cps	a_i, G
$Ni(i\text{-}C_3H_7\text{–}t\text{-}C_4H_9HCH_3)_2$[b]	α	+2349	−0.334
	β	+5995	−0.853
	γ	−158	+0.0225
$Ni(i\text{-}C_3H_7\text{–}CF_3HCH_3)_2$	α	+1771	−0.225
	β	+5182	−0.747
$Ni(i\text{-}C_3H_7\text{–}NapHCH_3)_2$	α	+2110	−0.316
	β	+5880	−0.880
$Ni(i\text{-}C_3H_7\text{–}C_6H_5HH)_2$	β	+4934	−0.835

[a] Data were obtained at ~30° and refer to 60 Mcps. [b] Slightly impure sample; spectrum indicates no exchange between complex and free ligand contaminant; coupling constants calculated assuming N_t = 1 and μ_t = 3.35 BM.

Spectral Measurements.—Electronic spectra were recorded on a Cary Model 14 spectrophotometer. (Data and spectra of interest are presented in Table V and Figure 2.)

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Results

The synthetic methods for preparing α,β-unsaturated β-ketoamines are sufficiently flexible that complexes of **1** can be obtained with a considerable variety of chelate ring substituents. As in a recent publication,[13f] bis(β-ketoamino) complexes are designated as $M(R\text{–}R_\gamma R_\beta R_\alpha)_2$, the substituents being listed in order starting with that on nitrogen. The stereochemical populations reflecting the positions of equilibria 1 and 2 are primarily affected by the nature of R; the other ring substituents have a detectable but secondary effect.[15,16] Large R groups can introduce considerable steric strain in the *trans*-planar form which is somewhat relieved if the complex undergoes a torsional distortion to a pseudo-tetrahedral structure.[24]

A direct comparison of the relative stabilities of planar–tetrahedral Co(II) compared to planar–tetrahedral Ni(II) is made difficult by the observation in this and past work[16] that equilibria 1 and 2 do not occur to a measurable extent for complexes of the *same* ligand. With reference to **1**, equilibrium 2 obtains only when R = H whereas equilibrium 1 is produced by R = CH_3, *n*-alkyl, or aryl[15,16] but not by R = H. Larger R groups such as *i*-C_3H_7 usually produce exclusively tetrahedral complexes. The situation is summarized by the statement that in noncoordinating solvents Co(II) complexes with R = CH_3 or larger are tetrahedral only and that Ni(II) complexes with R = H are exclusively planar up to at least 80°.[16] In view of these difficulties the closest possible comparison is that of the pair of equilibria 3 and 4, in which the

$$\text{planar } Ni(CH_3\text{–}R_\gamma R_\beta R_\alpha)_2 \rightleftharpoons \text{tetrahedral } Ni(CH_3\text{–}R_\gamma R_\beta R_\alpha)_2 \quad (3)$$

$$\text{planar } Co(H\text{–}R_\gamma R_\beta R_\alpha)_2 \rightleftharpoons \text{tetrahedral } Co(H\text{–}R_\gamma R_\beta R_\alpha)_2 \quad (4)$$

smallest R group giving rise to the configurational equilibrium for nickel is employed in (3). Because of the presumed close structural similarity of the species involved, a reasonable assumption at the outset is that after correction for electronic factors $\Delta S(3) \cong \Delta S(4)$ and that the energy differences between the configurations of each metal would be dominated by enthalpy effects. Further, the same kinds of contributions to ΔH should be present in (3) and (4), although not necessarily in the same proportion to the total enthalpy change of each reaction. In order to assess the relative energies of Ni(II) and Co(II) in their two configurations, the thermodynamic values (ΔG, ΔH, ΔS) for the planar → tetrahedral structural change in solution for a series of equilibrium pairs (3)–(4) have been determined.

In principle the number of Co–Ni equilibrium pairs which might be compared is limited only by the variety of sets of R_α, R_β, R_γ substituents available. However, serious experimental difficulties were encountered in attempting to prepare all complexes necessary for the study of a given pair of equilibria. Comparisons are restricted to the six pairs A–F despite much effort to obtain additional examples

A $Co(H\text{–}CH_3HCH_3)_2\text{–}Ni(CH_3\text{–}CH_3HCH_3)_2$
B $Co(H\text{–}C_6H_5HCH_3)_2\text{–}Ni(CH_3\text{–}C_6H_5HCH_3)_2$
C $Co(H\text{–}t\text{-}C_4H_9HCH_3)_2\text{–}Ni(CH_3\text{–}t\text{-}C_4H_9HCH_3)_2$
D $Co(H\text{–}CH_3CH_3H)_2\text{–}Ni(CH_3\text{–}CH_3CH_3H)_2$
E $Co(H\text{–}CF_3HCH_3)_2\text{–}Ni(CH_3\text{–}CF_3HCH_3)_2$
F $Co(H\text{–}NapHCH_3)_2\text{–}Ni(CH_3\text{–}NapHCH_3)_2$

(Nap is β-naphthyl.) Pairs A and B have been completely specified in terms of the thermodynamics of their configurational changes in recent work.[16] The establishment of equilibria 3 and 4 and the method of procedure for obtaining the thermodynamic quantities of the pairs of equilibria follow the detailed exposition given elsewhere[16] and are summarized in the following two sections.

Equilibrium 3: Establishment and Thermodynamics of the Configurational Change.—For the equilibria 3 and 4 $\Delta G = -RT \ln K_{eq}$ and $K_{eq} = N_t/N_p$, with N_t and N_p the mole fractions of tetrahedral and planar forms, respectively. For 3 it is easily shown that

$$N_t = [\exp(\Delta G/RT) + 1]^{-1} = \mu_{obsd}^2/\mu_t^2 \qquad (5)$$

in which μ_{obsd} is the observed moment of the equilibrium mixture and μ_t the limiting moment of the tetrahedral form; both are calculated from the Curie law.

$Ni(H\text{–}R_\gamma R_\beta R_\alpha)_2$ complexes relevant to the pairs A–E showed no proton contact shifts up to 80° and are concluded to have $N_p = 1$; $Ni(H\text{–}NapHCH_3)_2$ was not prepared because the very low solubility of the cobalt analog (*vide infra*) implied that this complex would be insufficiently soluble for pmr measurements. $Ni(CH_3\text{–}R_\gamma R_\beta R_\alpha)_2$ complexes in the pairs A–F all showed small proton contact shifts which increased with increasing temperature, consistent with an endothermic displacement of (3) to the right. The contact shifts were measured over a temperature range and interpreted according to eq 6 in which the symbols

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SkT}N_t \qquad (6)$$

have their usual meanings.[15] The electron–nuclear coupling constants a_i and the g values for the tetrahedral forms of $Ni(CH_3\text{–}R_\gamma R_\beta R_\alpha)_2$ were obtained from the corresponding $Ni(i\text{-}C_3H_7\text{–}R_\gamma R_\beta R_\alpha)_2$ complexes, which have $N_t = 1$ or are sufficiently paramagnetic that N_t can be determined accurately from eq 5. Magnetic moments, contact shifts, and coupling constants determined for the latter species are set out in

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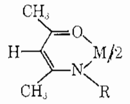
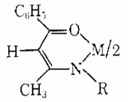
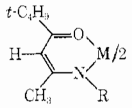
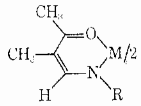
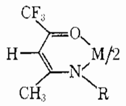
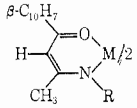
[24] Evidence is accumulating that steric compression in complexes with an over-all planar structure can be alleviated by other than a torsional distortion. Recent pertinent examples include bis(N-ethylsalicylaldimino)-nickel(II)[25] and bis(N-phenyl-N′-*p*-tolyl-C-methylformazyl)nickel(II),[26] which have a "folded" or "stepped" structure in which the coordination sphere is planar and the two chelate rings are disposed in mean parallel planes separated by ~1–2 Å. Structures such as this may apply to molecules which we describe here or have described in past articles on configurational equilibria as "planar." This structure and ones in which the chelate rings are approximately or exactly planar are not distinguishable by magnetic or spectral measurements of the sort employed here, but these are distinguishable from pseudo-tetrahedral Co(II) and Ni(II) structures, which have different ground-state spin multiplicities.

(25) L. M. Shkol'nikova, A. N. Knyazeva, and V. A. Voblikova, *Zh. Strukt. Khim.*, **8**, 94 (1967).

(26) D. Dale, *J. Chem. Soc., Sect. A*, 278 (1967).

TABLE IV

THERMODYNAMIC VALUES FOR THE PLANAR ⇄ TETRAHEDRAL INTERCONVERSION

Structure	Pair	R	M	Temp range, °K[a]	ΔH, cal/mole	ΔS, cal/mole deg	$\Delta G_{298°K}$, cal/mole	$N_{t,\ 298°K}$
	A	H	Co	240–345	706 ± 60	4.62 ± 0.50	−671 ± 100	0.76
		CH_3	Ni	230–350	2950 ± 10	3.98 ± 0.20	1770 ± 70	0.048
					ΔΔH ≅ −2240	ΔΔS = 0.64	ΔΔG ≅ −2440	
	B	H	Co	235–330	1640 ± 60	5.96 ± 0.60	−136 ± 100	0.56
		CH_3	Ni	240–360	4810 ± 10	8.22 ± 0.20	2360 ± 70	0.018
					ΔΔH = −3170	ΔΔS = −2.26	ΔΔG ≅ −2500	
	C	H	Co	235–325	2800 ± 30	7.63 ± 0.05	526 ± 50	0.29
		CH_3	Ni	290–380	5080[c]	7.80[c]	2760[c]	0.009
					ΔΔH = −2280	ΔΔS = −0.17	ΔΔG ≅ −2230	
	D	H	Co	240–310	1910 ± 150	4.15 ± 0.70	673 ± 120	0.24
		CH_3	Ni	340–400	5620[c]	3.92[c]	4450[c,d]	0.0005
					ΔΔH = −3710	ΔΔS = 0.23	ΔΔG ≅ −3780	
	E	H	Co	230–340	~0	1.41 ± 0.20	−420 ± 60	0.67
		CH_3	Ni	290–375	2760 ± 10	4.11 ± 0.20	1540 ± 70	0.069
					ΔΔH = −2760	ΔΔS = −2.70	ΔΔG = −1960	
	F	H	Co		e	e	e	0.36[f]
		CH_3	Ni	330–375	2300 ± 10	1.56 ± 0.10	1840 ± 40[d]	0.043

[a] Range of observation for which ΔG is a linear function of temperature. [b] Obtained from nmr or susceptibility data unless otherwise indicated. [c] Errors not estimated owing to uncertainty in coupling constants (see text). [d] Extrapolated value. [e] Complex is insufficiently soluble for measurement. [f] Estimated from integration of electronic spectrum.

Tables II and III. Magnetic moments of the R = CH_3 complexes are much too small to be accurately measurable and are not given. Free energy changes at the various temperatures of contact shift measurement were calculated from eq 6 and enthalpy and entropy changes were derived from a least-squares fit of the experimental ΔG results *vs.* temperature according to $\Delta G = \Delta H - T\Delta S$. The basic assumptions in this procedure are that a_i values are temperature independent and that the geometries of tetrahedral $Ni(i\text{-}C_3H_7\text{–}R_\gamma R_\beta R_\alpha)_2$ and $Ni(CH_3\text{–}R_\gamma R_\beta R_\alpha)_2$ are sufficiently similar that the accurately determined a_i values of the former can be transferred to the latter. There exists good evidence that in tetrahedral nickel complexes coupling constants are not significantly dependent on the nature of the R group.[15] The only exception to this procedure involved $Ni(CH_3\text{–}CH_3CH_3H)_2$. $Ni(i\text{-}C_3H_7\text{–}CH_3CH_3H)_2$ could not be prepared in an adequate state of purity and the a_α coupling constant was obtained from the structurally similar complex $Ni(i\text{-}C_3H_7\text{–}CH_3HH)_2$.[15]

Values of ΔG, ΔH, and ΔS for the nickel complexes in the pairs A–F are given in Table IV. Plots of the experimental ΔG values *vs.* temperature are shown in Figure 1. The linear dependences observed provide strong evidence for the existence of equilibrium 3. Deviations from linearity at lower temperatures in several cases arise from the presence of associated, paramagnetic species over which the contact shifts are also averaged.[13,15] Extreme behavior of this sort was encountered with $Ni(CH_3\text{–}C_6H_5HH)_2$, whose apparent ΔG values were nonlinear with temperature from 300 to 365°K, indicating substantial molecular association in this temperature interval and thwarting an attempt to study the equilibrium pair of complexes with the C_6H_5HH ligand structure.

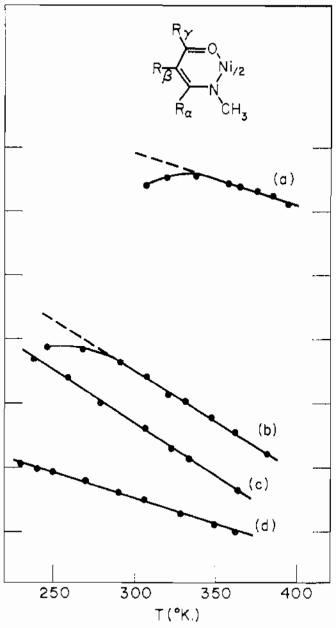


Figure 1.—Temperature dependence of the free energy changes for the planar–tetrahedral conversion of nickel(II) complexes in $CDCl_3$ solution: (a) $Ni(CH_3\text{–}CH_3CH_3H)_2$, (b) $Ni(CH_3\text{–}t\text{-}C_4H_9\text{-}HCH_3)_2$, (c) $Ni(CH_3\text{–}C_6H_5HCH_3)_2$, (d) $Ni(CH_3\text{–}CH_3HCH_3)_2$.

Equilibrium 4: Establishment and Thermodynamics of the Configurational Change.—Spectral and magnetic observations of $Co(R\text{–}R_\gamma R_\beta R_\alpha)_2$ complexes, given in Tables II and V, parallel closely those previously reported.[16] First, the new R = CH_3 species have moments in the solid and solution phases which differ by 0.1 BM or less and fall in the 4.2–4.5-BM range characteristic of tetrahedral β-ketoamine complexes with R = alkyl and aryl. Their ligand field spectra are entirely typical of the pseudo-tetrahedral configuration.[16] These complexes are concluded to have $N_t = 1$ in solution. Second, the three R = H complexes, $Co(H\text{-}t\text{-}C_4H_9HCH_3)_2$ $Co(H\text{-}CF_3HCH_3)_2$, and $Co(H\text{-}NapHCH_3)_2$ are all low spin and planar in the solid. The first two complexes in solution have moments intermediate between their solid-state values and the lower tetrahedral limit of ~4.2 BM. $Co(H\text{-}NapHCH_3)_2$ is insufficiently soluble for a solution magnetic measurement. Ligand field spectra of the R = H members of pairs A, B, D, and E have been published.[16] The solution spectra of $Co(H\text{-}t\text{-}C_4H_9\text{-}HCH_3)_2$ and $Co(H\text{-}NapHCH_3)_2$, shown in Figure 2, are quite similar to these; their most significant feature is the retention of the band at ~8100–8600 cm^{-1}. A band in this region is found in the polycrystalline spectra of all $Co(H\text{-}R_\gamma R_\beta R_\alpha)_2$ complexes and is characteristic of the low-spin, planar configuration. The spectral intensities of solutions containing $Co(H\text{-}CF_3HCH_3)_2$ and $Co(H\text{-}t\text{-}C_4H_9HCH_3)_2$ show a strict adherence to Beer's law in the 0.001–0.070 *M* range, which includes concentrations used in magnetic measurements. The R = H complexes in pairs A, B, and D have also been shown to obey Beer's law.[16] For all R = H species associated forms are ruled out and the available evidence indicates that in solution $N_t < 1$.

TABLE V

LIGAND FIELD SPECTRAL DATA[a]

Complex	Medium[b]	λ_{max}, cm^{-1} (ϵ_M)[c]	
$Co(H\text{-}t\text{-}C_4H_9HCH_3)_2$	$CHCl_3$		10,400 sh 8400 (21)
$Co(CH_3\text{-}CF_3HCH_3)_2$	$CHCl_3$	21,600 sh	11,000 sh 8260 (46)
	Mull	21,300 sh	10,650 sh 8150
$Ni(i\text{-}C_3H_7\text{-}C_6H_5HH)_2$			
Brown	Mull		10,600 sh 9100–5500
Green	Mull	16,000 sh	
$Co(H\text{-}NapHCH_3)_2$	$CHCl_3$		10,900 sh 8470 (25) 7400 sh
	Mull		9,100 sh 8550
$Co(CH_3\text{-}NapHCH_3)_2$	$CHCl_3$		11,000 sh 8300 (42)

[a] All data obtained at room temperature. [b] Mull spectra taken in Kaydol. [c] sh = shoulder.

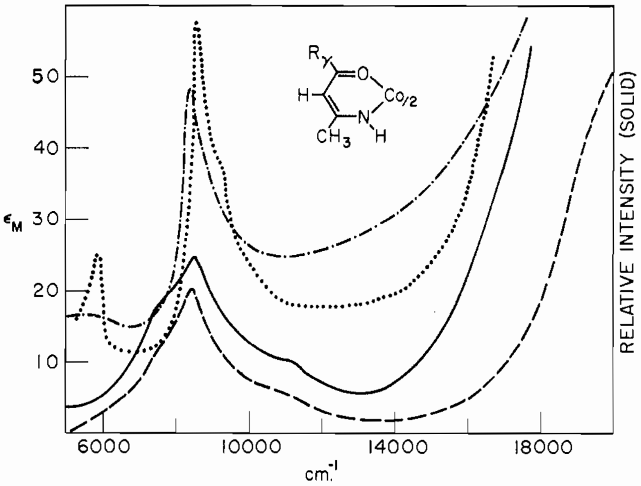


Figure 2.—Ligand field spectra of cobalt(II) complexes. $Co(H\text{-}NapHCH_3)_2$: ———, chloroform solution, 25°; ......, hydrocarbon mull. $Co(H\text{-}t\text{-}C_4H_9HCH_3)_2$: – – – –, chloroform solution, 25°; ·–·–·–, hydrocarbon mull.

Free energy changes for the structural conversion of the cobalt(II) complexes were evaluated from measurement of the temperature dependence of the magnetic susceptibilities according to eq 7,[16] in which μ_p

$$\Delta G = RT \ln \left[\frac{\mu_t^2 - \mu_{obsd}^2}{\mu_{obsd}^2 - \mu_p^2} \right] \tag{7}$$

is the moment of the planar form. Values of μ_p were taken as the moments of the polycrystalline solids at room temperature, and 4.38 BM, an average value for the exclusively tetrahedral $Co(R\text{-}R_\gamma R_\beta R_\alpha)_2$ complexes (R = CH_3, alkyl),[16] was used for μ_t. The ΔG values for the four cobalt complexes in pairs A–D varied linearly with temperature as shown in Figure 3; deviation of the high-temperature points is believed due to decomposition. Values of ΔH and ΔS were obtained from a least-squares fit of ΔG *vs.* *T*. Experimental magnetic moments and ΔG values for $Co(H\text{-}t\text{-}C_4H_9HCH_3)_2$ are set out in Table VI; similar tabulations for the other three complexes have been given previously.[16] The thermodynamic data for the cobalt complexes in pairs A–E are listed in Table IV. Because of its low solubility, thermodynamic data for $Co(H\text{-}NapHCH_3)_2$ could not be determined. The value of N_t given in Table IV was estimated by integration of spectral intensities using the procedure described earlier.[16]

The data in Table IV show that the planar–tetrahedral structural change for $Co(H\text{-}R_\gamma R_\beta R_\alpha)_2$ is endothermic. The only exception appears to be $Co(H\text{-}CF_3HCH_3)_2$, which has a temperature-independent moment of 3.78 ± 0.10 BM in the 230–340°K. range. The room-temperature moment was checked by two independent methods (*cf.* Table II) on several different preparations and good agreement was obtained. Because the complex is monomeric according to Beer's law measurements, it is concluded that equilibrium 4 obtains and that $\Delta H \sim 0$. This result is probably due to an intrinsically positive enthalpy change for the structural conversion which is fortuitively cancelled by a negative solvation enthalpy change.

Structural Conversion in the Solid Phase.—$Ni(i\text{-}C_3H_7\text{-}C_6H_5HH)_2$ is unlike any other β-ketoamine complex of Ni(II) with R = $i\text{-}C_3H_7$ inasmuch as it is obtained as a green, diamagnetic solid by the standard preparative and purification procedure. If this planar modification is heated at 100° for several hours, a brown, crystalline, paramagnetic material is obtained whose mull spectrum (Table V) shows the broad near-infrared feature characteristic of pseudo-tetrahedral β-ketoamine complexes. This material has moments of

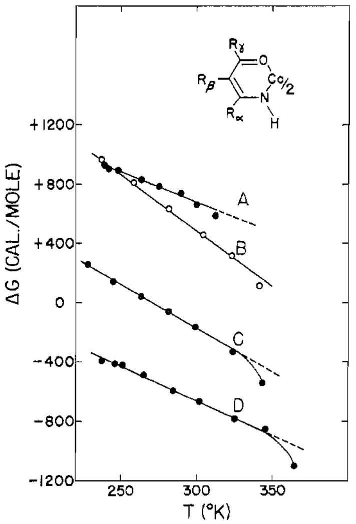


Figure 3.—Temperature dependence of the free energy changes for the planar–tetrahedral conversion of cobalt(II) complexes in $CHCl_3$–TMS solution: A, Co(H–$CH_3CH_3H)_2$; B, Co(H–*t*-C_4H_9-$HCH_3)_2$; C, Co(H–$C_6H_5HCH_3)_2$; D, Co(H–$CH_3HCH_3)_2$.

Table VI

Temperature Dependence of the Planar-Tetrahedral Equilibrium of Co(H–*t*-$C_4H_9HCH_3)_2$ in Chloroform Solution

Temp, °K	μ_{eff}, BM[a,b]	ΔG, cal/mole[c]
237	2.67	963
258	2.81	810
281	2.98	634
304	3.15	456
323	3.28	311
341	3.44	108[d]

[a] Nmr method; $CHCl_3$ with 15% v/v TMS used as solvent. [b] Estimated error ±2%. [c] Estimated error ±18% assuming no uncertainty in μ_p and μ_t. [d] Deviation of ΔG *vs.* T linearity due to decomposition (*cf.* Figure 3).

2.95 (solid) and 3.05 BM (chloroform solution). Both of these are considerably less than the moments of Ni(*t*-C_4H_9–$C_6H_5HH)_2$ (3.27 BM, solid; 3.25 BM, $CHCl_3$),[13f] indicating incomplete conversion to the tetrahedral configuration. After an induction period of 1 week, the susceptibility of the crystalline brown form was observed to decrease linearly with time. This behavior is caused by a tetrahedral → planar conversion because the decrease in paramagnetism is accompanied by a color change to the original green. Magnetic measurements have led to the simple rate expression $N_t = 0.93 - 0.12t$ (assuming $\mu_t = 3.27$ BM) and the "rate constant" 0.12/week. The planar → tetrahedral structural conversion has been effected for Ni(C_2H_5–$C_6H_5HCH_3)_2$ by heating[15] and Ni(*sec*-C_4H_9–$C_6H_5HH)_2$ has been isolated as a 1:1 mixture of planar and tetrahedral isomers.[13f] These results show that in the crystalline phase as well as in solution the energy difference between the planar and tetrahedral configurations may be quite small.

Discussion

Comparative Stereochemical Populations and Thermodynamics.—The complete set of thermodynamic results for 11 nickel and cobalt complexes in pairs A–F is presented in Table IV. Values of N_t at 298°K were calculated from the corresponding ΔG data except in the case of Co(H–Nap$HCH_3)_2$, for which the N_t value given is only an estimate. Quantitative comparisons of ΔG, ΔH, ΔS, and N_t can be made for the pairs A–E.

The plot shown in Figure 4 reveals that the stereochemical populations for members of the pairs A–D are monotonically related to one another while those of pairs E and F do not fit the pattern. The significance of the point for pair F is questionable because N_t(Co) is not known accurately. The cause of the deviation of pair E from this pattern is not known; possibly one of the equilibria is more susceptible to specific solvent effects than the other. However, the deviation of pair E from the over-all trend is not large, and it is concluded that *the stereochemical populations of Ni(CH_3–$R_\gamma R_\beta R_\alpha)_2$ and Co(H–$R_\gamma R_\beta R_\alpha)_2$ in chloroform solution generally run parallel to each other.* For every pair N_t(Co) ≫ N_t(Ni) even though the nickel complexes have the larger R group. Hence, if quantitative comparisons of equilibria 3 and 4 could actually be made for complexes with identical R groups, there is no doubt that the large inequality in stereochemical populations would hold.

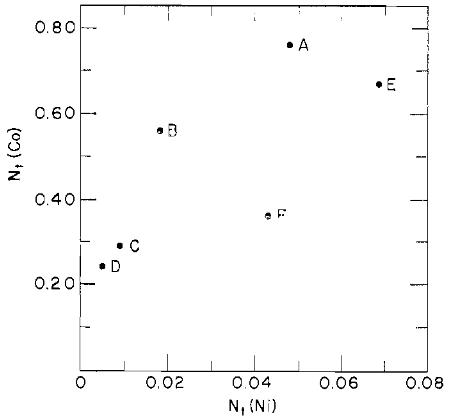


Figure 4.—Stereochemical correlation of Co(H–$R_\gamma R_\beta R_\alpha)_2$–Ni($CH_3$–$R_\gamma R_\beta R_\alpha)_2$ pairs at 298°K in solution. The pairs are defined in the text and Table IV. N_t = mole fraction of tetrahedral form as obtained from pmr or magnetic susceptibility data.

The relative thermodynamic changes for the structural conversions in (3) and (4) are most simply expressed as ΔΔ quantities (*e.g.*, $\Delta\Delta H = \Delta H_{Co} - \Delta H_{Ni}$), which are given in Table IV. The values of ΔG express the different tendencies of the cobalt (R = H) and nickel (R = CH_3) complexes to assume their tetrahedral configurations at the specified temperature. If the configurational equilibria of Ni(II) and Co(II) complexes with identical ligands could be studied, the corresponding ΔΔ quantities would furnish the basis for a rigorous quantitative comparison and interpretation of stereochemical tendencies. It is therefore necessary to establish the effect of the same and different R groups on these quantities and to investigate the factors responsible for the marked inequality in the stereochemical populations of $Co(H\text{–}R_{\gamma}R_{\beta}R_{\alpha})_2$ and $Ni(CH_3\text{–}R_{\gamma}R_{\beta}R_{\alpha})_2$, the direction of which is the same as if identical R groups were present.

Effects of R Groups on $\Delta\Delta S$.—If Co(II) and Ni(II) complexes were compared in strictly noncoordinating solvents, the only important contribution to $\Delta\Delta S$ would presumably be the difference in the electronic entropy changes $R \ln 2 - R \ln 3 = 1.38 - 2.18 = -0.80$ eu, assuming orbitally nondegenerate ground states. The observed $\Delta\Delta S$ quantities differ from this number in value and, for two cases, in sign. After correction for the electronic entropy changes, the individual ΔS values are all positive. A possible explanation for this behavior is that the planar configuration is the more strongly solvated in most cases and that irregular solvation effects in addition to $\Delta\Delta S_{\text{elec}}$ contribute to $\Delta\Delta S$. For pairs A–D the $T\Delta\Delta S$ contribution to $\Delta G_{298°}$ ranges from $\sim$2 to 27%. For pair E the contribution is $\sim$40% but the value of $|T\Delta\Delta S|$ is less than one-third of $|\Delta\Delta H|$. Thus for pairs A–E the sign and magnitude of $\Delta\Delta G$ are determined primarily by the sign and magnitude of $\Delta\Delta H$, a conclusion which surely would apply to the case of identical R groups.

If the individual contributions to ΔH and $\Delta\Delta H$ could be evaluated, it should then be possible to specify the principal factor(s) responsible for the greater tendency of Co(II) to assume the tetrahedral configuration. As the following discussion reveals, it is usually not possible to evaluate these contributions even semiquantitatively. Nonetheless, because the configurational equilibria 1 and 2 are now of rather widespread occurrence,[12–16] it appears useful to set out the individual contributions to ΔH for any such equilibrium, and to attempt an assessment of each for the specific cases of equilibria 3 and 4.

Contributions to ΔH and $\Delta\Delta H$.—The contributions to the observed enthalpy change ΔH for a given cobalt or nickel complex in solution are indicated in the following thermodynamic cycle (L = ligand)

$$\begin{tikzcd}
ML_2(\text{planar, g}) \arrow[r, "\Delta H_{M}{}^{t-p}\ (8)"] \arrow[d, "\Delta H_{M}{}^{p}(\text{soln})"] & ML_2(\text{tetrahedral, g}) \arrow[d, "\Delta H_{M}{}^{t}(\text{soln})"] \\
ML_2(\text{planar, soln}) \arrow[r, "\Delta H"] & ML_2(\text{tetrahedral, soln})
\end{tikzcd}$$

From the cycle

$$\Delta H = -\Delta H_{M}{}^{p}(\text{soln}) + \Delta H_{M}{}^{t}(\text{soln}) + \Delta H_{M}{}^{t-p}(\text{g}) \qquad (8)$$

in which $\Delta H_{M}{}^{t-p}(\text{g})$ is the enthalpy change for the gas-phase planar–tetrahedral conversion, and $\Delta H_{M}{}^{p}(\text{soln})$ and $\Delta H_{M}{}^{t}(\text{soln})$ are the enthalpies of solution of the gaseous planar and tetrahedral forms, respectively. For a Co–Ni pair

$$\Delta\Delta H = -\Delta\Delta H_{\text{Co–Ni}}{}^{p-p}(\text{soln}) + \Delta\Delta H_{\text{Co–Ni}}{}^{t-t}(\text{soln}) + \Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{g}) \qquad (9)$$

None of the terms on the right-hand side of (9) can be evaluated experimentally. The first two would be expected to be very nearly zero for complexes with identical R groups if the solvent is noncoordinating. When R = H and CH_3 and the solvent is chloroform, these terms are considered to be negligibly small because they represent differences in solvation enthalpies of molecules with the same over-all size and shape.[27] Hence, it is reasonable to assume that

$$\Delta\Delta H \cong \Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{g}) \qquad (10)$$

for processes 3 and 4. The gas-phase enthalpy change may be decomposed into a number of individual contributions which for a Co–Ni pair may be expressed as

$$\Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{g}) = \Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{L}) + \Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{L–L}) + \Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{M–L}) + \Delta H_{\text{Co–Ni}}{}^{t-p}(\text{CFSE}) \qquad (11)$$

The evaluation of several of the terms on the right-hand side of eq 11 would be aided by detailed structural information, but the very limited amount of X-ray results for bis(β-ketoamine) complexes is confined to Ni(II) species[28] for which no molecular parameters have been reported. Pertinent structural information is drawn from bis(salicylaldimines) whose chelate ring dimensions should be very similar to those of β-ketoamine complexes of the same metal with the same over-all structure.

The first term in eq 11 expresses the enthalpy difference due to changes in ligand bond angles and distances in the two configurations and will be nonzero if the cobalt and nickel complexes experience these changes to a different extent. The value of this term is certain to be very small when the ligand structures are as similar as $H\text{–}R_{\gamma}R_{\beta}R_{\alpha}$ and $CH_3\text{–}R_{\gamma}R_{\beta}R_{\alpha}$[29–31] and is neglected. The second term is due to enthalpy differences derived from intramolecular ligand–ligand interactions in the planar and tetrahedral configurations of the two metals. Because the mean planes of the chelate rings in the tetrahedral forms are approximately orthogonal,[31] any significant interactions of this type are believed to be restricted to the *trans*-planar structure[32–34] and are expected to take the form of hydrogen bonding between R and the adjacent chelate ring oxygen. Strong interactions of this sort are undoubtedly present in *trans*-planar bis(salicylaldoximino)copper(II)[35] and -nickel(II)[36] in which the interligand O···O distances vary from 2.52 to 2.63 Å and in which a nearly linear O–H···O hydrogen bond is likely. From the structure of bis(salicylaldimino)nickel(II),[33] the interligand N···O distance is estimated to

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(27) The only reported enthalpies of solution of four-coordinate complexes fitting this description are those of tetrahedral $Co(py)_2I_2$ and $Ni(py)_2I_2$ dissolved in chloroform; the values differ by 0.4 ± 0.3 kcal/mole.[3]

(28) (a) M. Dobler, *Helv. Chim. Acta*, **45**, 1628 (1962); (b) G. E. Gurr, *Inorg. Chem.*, **3**, 614 (1964).

(29) In this connection it is observed that ligand bond distances and angles for planar bis(3-methyl-N-isopropylsalicylaldimino)nickel(II)[30] and pseudo-tetrahedral bis(N-isopropylsalicylaldimino)nickel(II)[31] differ by no more than 0.02 Å and $\leqslant 4°$, respectively; the "bites" differ by only 0.13 Å. From this comparison we infer that $\Delta H_{\text{Ni}}{}^{t-p}$ could not exceed several kilocalories per mole and that $\Delta\Delta H_{\text{Co–Ni}}{}^{t-p}(\text{L})$ must be essentially zero.

(30) R. L. Braun and E. C. Lingafelter, *Acta Cryst.*, **21**, 546 (1966).

(31) M. R. Fox, P. L. Orioli, E. C. Lingafelter, and L. Sacconi, *ibid.*, **17**, 1159 (1964).

(32) X-Ray results have proven this structure for crystalline $Ni(H\text{–}C_6H_5HCH_3)_2$,[28b] bis(salicylaldimino)nickel(II),[33] and bis(N-methylsalicylaldimino)nickel(II).[34] The planar forms of $Ni(R\text{–}R_{\gamma}R_{\beta}R_{\alpha})_2$ (R = H, CH_3) and $Co(H\text{–}R_{\gamma}R_{\beta}R_{\alpha})_2$ are assumed *trans* in solution.

(33) J. M. Stewart and E. C. Lingafelter, *Acta Cryst.*, **12**, 842 (1959).

(34) (a) E. Frasson, C. Panattoni, and L. Sacconi, *J. Phys. Chem.*, **63**, 1908 (1959); (b) M. R. Fox and E. C. Lingafelter, *Acta Cryst.*, **22**, 943 (1967).

(35) M. A. Jarski and E. C. Lingafelter, *ibid.*, **17**, 1109 (1964); P. L. Orioli and E. C. Lingafelter, *ibid.*, **17**, 1113 (1964).

(36) L. L. Merritt, C. Guare, and A. E. Lessor, *ibid.*, **9**, 253 (1956).

be ~2.5 Å in $Co(H\text{–}R_\gamma R_\beta R_\alpha)_2$. However, the H–N···O angle of ~65° requires an H···O distance of ~2.3 Å compared to distances of ~1.8–1.9 Å in strong, linear N–H···O bonds.[37] For a number of bis(N-alkylsalicylaldimino) complexes with planar $M\text{–}O_2N_2$ coordination units the interligand α-C(R)···O distances are less than the sum of the van der Waals radii.[38] The $H_3C\cdots O$ distance in bis(N-methylsalicylaldimino)nickel(II) is 2.68 Å and the possibility of a C–H···O hydrogen bond has been considered.[34a] The conclusion drawn from these results is that hydrogen bonding in planar R = CH_3 and H complexes is a possibility but that the bond energies are low, perhaps no more than 1–2 kcal/mole, which is a reasonable upper limit for $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{L–L})$. For the case of identical R groups this term must be essentially zero.

The term $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{M–L})$ in eq 11 arises as a consequence of whatever differences exist between the total metal–ligand bond energies of the planar and tetrahedral configurations of each metal. At present there is no reliable way to estimate the value of this quantity. To the extent that bond lengths reflect bond energies, $\Delta H_{\text{M}}{}^{\text{t–p}}(\text{M–L})$ will be positive since the high-spin form of a given metal ion generally has a larger ionic radius than the low-spin form. This is the situation found in a comparison of tetrahedral bis(N-isopropylsalicylaldimino)-[31] and bis(3-ethyl-N-isopropylsalicylaldimino)nickel(II)[39] with planar bis(3-methyl-N-isopropylsalicylaldimino)nickel(II)[30] for which the Ni–O and Ni–N distances are 0.05–0.06 Å longer in the tetrahedral complex. $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{M–L})$ is expected to be nonzero when the R groups are the same and will presumably be somewhat larger when they are different. Indirect thermodynamic assessments indicate that mean metal–ligand bond energies increase slightly from cobalt to nickel in tetrahedral complexes.[4b,40] M–N bond distances are 0.05–0.06 Å larger in tetrahedral bis(N-*t*-butylpyrrole-2-aldimino)-cobalt(II) than in the *isostructural* Ni(II) analog.[41] If these same trends hold in planar complexes, the probable order of M–L bond energies is planar Ni > planar Co > tetrahedral Ni > tetrahedral Co. Unfortunately, the existing information is insufficient to fix the sign or magnitude of $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{M–L})$.

The remaining term in eq 11 represents the relative change in the CFSE's of the cobalt and nickel complexes as a consequence of the structural conversion and is given by

$$\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{CFSE}) = \Delta(\text{CFSE})_{\text{Co}}{}^{\text{t–p}} - \Delta(\text{CFSE})_{\text{Ni}}{}^{\text{t–p}} \quad (12)$$

The interpretation of the $\Delta\Delta H$ quantities in Table IV is complicated by the contribution of three terms, $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{L–L})$, $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{M–L})$, and $\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{CFSE})$. Of the three we suggest, but cannot prove, that the first is the smallest. Because the structural equilibrium for $Ni(H\text{–}R_\gamma R_\beta R_\alpha)_2$ is unobservable by the exceedingly sensitive contact shift method, it is safely estimated that at 300°K $K_{\text{eq}} < 0.01$ and $\Delta G >$ 2.8 kcal/mole. Taking $\Delta S = +4$ eu as a representative value, $\Delta H > 4$ kcal/mole for the unobserved structural change. If a comparison of cobalt and nickel complexes with R = H is made, $\Delta\Delta H$ would be a negative number of the order of a few kilocalories per mole (the range of observed values for reactions 3 and 4) or more. The observed values of $\Delta\Delta H$, derived from measurable equilibria, agree in sign and, roughly, in magnitude with the case in which $\Delta\Delta H_{\text{Co–Ni}}{}^{\text{t–p}}(\text{L–L})$ can legitimately be neglected but the two remaining terms cannot. On this basis the $\Delta\Delta H$ values are concluded to arise principally from bond strength differences and CFSE effects.

A desirable procedure at this point would be to correct the observed $\Delta\Delta H$ values for CFSE effects, as has been done in interpretations of the relative stabilities of tetrahedral and octahedral complexes as a function of the coordinated metal.[3,4] In this way the stability differences between the stereoisomers of the two metals apart from CFSE effects could be estimated. Values of $(\text{CFSE})_{\text{Co}}{}^{\text{t}} \sim 17$ and $(\text{CFSE})_{\text{Ni}}{}^{\text{t}} \sim 9.2$ kcal/mole are readily obtained.[42] Unfortunately, the required $(\text{CFSE})_{\text{M}}{}^{\text{p}}$ values cannot be satisfactorily estimated at present because of the uncertainty in the ground-state electronic structures and ligand field spectral assignments of the planar Co(II) and Ni(II) complexes.

Summary

The following principal conclusions are drawn from the results of this investigation and serve to substantiate and extend those presented earlier.[16]

(i) Ligands which stabilize a measurable amount of tetrahedral Ni(II) produce ~100% tetrahedral Co(II), while ligands which stabilize a measurable amount of planar Co(II) produce ~100% planar Ni(II) under the same conditions of solvent and temperature.

(ii) In those cases for which the planar–tetrahedral configurational equilibrium can be directly measured, the stereochemical populations of Co(II) and Ni(II) complexes with minimal ligand structural differences generally show a monotonic relationship.

(iii) The relative positions of the equilibria in (ii) are mainly controlled by enthalpy effects; entropy changes (in chloroform) favor the formation of the tetrahedral isomers.

(iv) The stability (enthalpy) difference between tetrahedral and planar Ni(II) is ~2–4 kcal/mole greater than that between tetrahedral and planar Co(II) for β-ketoamine complexes of minimal ligand structural differences.

(v) The stability differences in (iv) derive principally from differences in the CFSE's and metal–ligand bond energies of Ni(II) and Co(II) in their

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[42] Values of $(\text{CFSE})_{\text{Co}}{}^{\text{t}}$ and $(\text{CFSE})_{\text{Ni}}{}^{\text{t}}$ ($^6/_5\Delta_{\text{t}}$ and $^4/_5\Delta_{\text{t}}$, respectively, in the one-electron approximation) may be estimated from the assigned[15,16] ν_2 and ν_3 transition energies of the tetrahedral configurations and the Liehr–Ballhausen diagrams for d^7 and d^8: A. D. Liehr and C. J. Ballhausen, *Ann. Phys.*, **6**, 134 (1959); A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963)

two stereoisomers. This conclusion should also apply to complexes with identical ligand structures. The observed variations of $\Delta\Delta H$ with ligand structure imply that $\Delta\Delta H_{\text{Co-Ni}}{}^{\text{t-p}}$(CFSE) is not the sole contributing factor to the stability differences. Values of stability differences corrected for CFSE effects could not be obtained.

Finally, the complexes $\text{Fe(R-C}_6\text{H}_5\text{HCH}_3)_2$ (R = H, CH_3) have been prepared and found to be tetrahedral in chloroform solution.[5] Provided that the planar configuration of these complexes possesses an energy minimum, this result, together with those reported herein, demonstrates that the relative stability of the planar form increases in the sequence Ni(II) > Co(II) > Fe(II). Further results concerning the four-coordinate stereochemistry of divalent ions other than Ni(II) and Co(II) will be reported in a future publication.

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Reactions of Coordinated Ligands. XVIII. Metal Ion Control in the Synthesis of Octahedral Nickel(II) Complexes of α-Diketobis(3-aminopropylimines)

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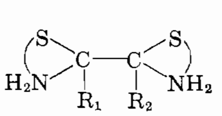
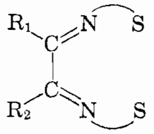
The reaction of α-diketones with 1,3-diaminopropane in the presence of nickel(II) salts yields a new family of chelate compounds. The new ligands 2,3-butanedionebis(3-aminopropylimine) (BTM), 2,3-pentanedionebis(3-aminopropylimine) (PTM), and 1,2-cyclohexanedionebis(3-aminopropylimine) (CTM) could not be prepared in the absence of the metal ion. The metal ion is six-coordinate in the thiocyanate and $ZnCl_4{}^{2-}$ derivatives, $NiL(NCS)_2$ and $NiL(ZnCl_4)$, and in solution in a variety of solvents. The ligands exert a strong ligand field, having an average $Dq^{xy} = 1228\ \text{cm}^{-1}$. Infrared spectra reveal that the thiocyanate anions are N bonded and occupy *trans* positions in the coordination sphere of the metal ion. Both symmetric and asymmetric stretching modes are observed for the $-N{=}\overset{|}{C}\overset{|}{C}{=}N-$ grouping.

Introduction

In recent years there has been an increased interest in the area of ligand reactions [2] This has been accompanied by a growing awareness of the fact that metal ions often permit the facile synthesis of coordinated ligands in cases where the free organic materials either are not accessible by separate synthesis or can be prepared only by lengthy and wasteful routes These developments have led to the characterization of several new categories of chelate derivatives. Examples of this type of process include: (1) the reaction of polyamines with ketones,[3] aldehydes,[3] hydroxy ketones,[4] α,β-unsaturated ketones,[4] and 2,6-diacetylpyridine;[5] (2) the reaction of coordinated mercaptides with dibromoalkanes;[6] and (3) the reaction of mercaptoamines with α-diketones.[7] Depending on the example, the latter reaction may proceed best by either the initial formation of a thiazolidine (I), which rearranges in the presence of a metal ion to give the corresponding Schiff base chelate (II),[8] or by condensation of the mercaptoamine and α-diketone in the presence of the metal ion.[7]

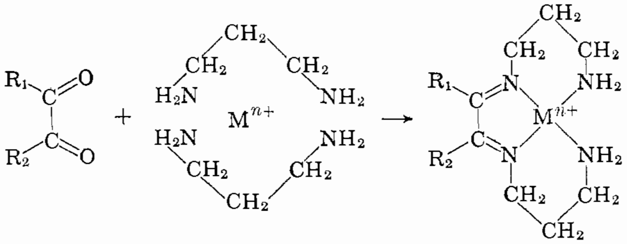


I



II

One of the more obvious routes to chelate ring formation is the reaction of a diamine with an α-diketone in the presence of a metal ion. Although a variety of early attempts to utilize this reaction failed to yield characterizable compounds,[9] we have succeeded in the synthesis of new chelate compounds by this method.



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