nickel complex is consistent with the low-temperature esr results[27] for benzene and *p*-dioxane clathrates of $NaNi(AA)_3$ which contain the same complex anion. The magnetic anisotropy of octahedral nickel(II) with an orbitally nondegenerate ground state is expected to be small.[5] This has been amply confirmed experimentally.[6,28]

$[Bu_4N][Co(AA)_3]$. Although the isotropic shifts for the tetrabutylammonium protons in this complex arise solely from the pseudo-contact interaction (eq 1), the labile equilibrium involved, as well as uncertainty in the relevant geometric factors, prevents an absolute evaluation of the anisotropy from the observed butyl proton resonance displacements. Qualitatively, results for both the cation and ligand pseudo-contact shifts indicate that $(K_{\parallel} - K_{\perp})$ is negative (*vide supra*), and therefore $K_{\perp} > K_{\parallel}$ in this compound. A rough quantitative evaluation of the susceptibility tensor anisotropy can be made from the estimated ligand proton pseudo-contact shifts using eq 1 and the calculated geometric factors. From a pseudo-contact shift of −1220 cps for the 3-hydrogen, a value of $K_{\parallel} - K_{\perp}$ of -3010×10^{-6} cgsu mole^{-1} at 34° is obtained. Since eq 1 applies to solids perhaps a better method, with some precedent,[29] is to compute g_{av} from the measured molar susceptibility with the equation given in ref 17 and then to use the equation,[4,18] $(\Delta\nu/\nu)_i = [-\beta^2 S(S+1)/45kT][(3\cos^2\chi_i - 1)/r_i^3][3g_{\parallel}^2 + g_{\parallel}g_{\perp} - 4g_{\perp}^2]$ to compute $g_{\parallel}$ and $g_{\perp}$. By this procedure we obtain $g_{av} = (^1/_3)(g_{\parallel} + 2g_{\perp}) = 2.55$, $g_{\parallel} - g_{\perp} = -0.57$ which yields $K_{\parallel} - K_{\perp} = -4280 \times 10^{-6}$ cgsu mole^{-1}. It should be emphasized that g tensor components obtained by this method are not comparable with those obtained from esr measurements at liquid helium temperatures where values of g_{av} near 4.5 are generally observed.[5,7] The magnetic susceptibility of octahedral cobalt(II) complexes does not obey the simple expression given in ref 17. Neither esr nor magnetic anisotropy measurements are available for compounds containing the $[Co(AA)_3]$ anion; however, our estimate is of the order of magnitude observed[30] for the magnitude anisotropy of cobalt(II) in Tutton salts at room temperature.

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Studies of the Planar–Tetrahedral Configurational Equilibrium in Solutions of Bis(β-ketoamino)cobalt(II) Complexes

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Abstract: A series of bis(β-ketoamino)Co(II) complexes of general formulation $Co[R_{\gamma}COCR_{\beta}C(NR)R_{\alpha}]_2$ has been synthesized by a nonaqueous chelation reaction. Only the tetrahedral stereoisomeric form is measurably populated in the solid and solution phases by complexes having $R_{\alpha} = CH_3$, $R_{\beta} = H$, $R_{\gamma} = CH_3$ and C_6H_5, and $R = CH_3$, n-C_3H_7, and C_6H_5. However, when R = H, three complexes having the following sets of substituents are low spin and planar in the solid but in solution exhibit magnetic and spectral properties indicative of the presence of both planar and tetrahedral forms: $R_{\alpha} = R_{\gamma} = CH_3$, $R_{\beta} = H$; $R_{\alpha} = CH_3$, $R_{\beta} = H$, $R_{\gamma} = C_6H_5$; $R_{\alpha} = H$, $R_{\beta} = R_{\gamma} = CH_3$. By a detailed study of spectral and magnetic properties over temperature and/or concentration ranges and consequent elimination of other solution equilibria known for bis(chelate)Co(II) complexes, it is concluded that these complexes are implicated in a planar ($S = {}^1/_2$) $\rightleftharpoons$ tetrahedral ($S = {}^3/_2$) configurational equilibrium similar to that already established for several classes of Ni(II) complexes but previously unknown for any other metal. Analysis of the temperature dependence of the magnetic moments has yielded ΔF, ΔH, and ΔS values characterizing the structural change for the three complexes. The formation of the tetrahedral stereoisomer is found to be endothermic in each case. Ni(II) complexes with R = H and having the same ligand systems are found to be 100% planar up to 80° in solution. Similar Ni(II) complexes with $R = CH_3$ are less than 5% tetrahedral at 25° whereas under the same conditions the corresponding Co(II) complexes are ~100% tetrahedral. The most important conclusions drawn from the data at hand are (i) ligands which stabilize a measurable amount of tetrahedral Ni(II) induce ~100% tetrahedral Co(II), and (ii) ligands which stabilize a measurable amount of planar Co(II) induce ~100% planar Ni(II). A brief comparison of thermodynamic data for the planar–tetrahedral conversion of Co(II) and Ni(II) complexes with R = H and CH_3 is presented.

The stereochemistry of complexes of cobalt(II) which are four coordinate on the basis of simplest formulation is frequently complicated in both the solution and solid phases by intermolecular association or additional intramolecular chelation. In solutions of noncoordinating solvents these effects are sometimes manifested by various types of structural equilibria involving high ($S = 3/2$) or low spin ($S = 1/2$) cobalt(II) which may be categorized as follows. The most

$$\text{octahedral polymer(s) (high spin)} \rightleftharpoons \text{tetrahedral (high spin)} \quad (1)$$

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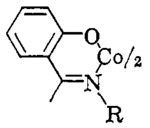
[1] (a) National Science Foundation Predoctoral Fellow, 1962–1966; (b) Alfred P. Sloan Foundation Fellow, 1964–1967.

prominent complex implicated in equilibrium 1 is bis(acetylacetonato)cobalt(II), originally proposed to be planar in solution,[2] but later found to be associated[3] and to consist of condensed octahedral tetrameric units in the crystal.[4]

Two other equilibria recognized at the outset of this study involve bis(N-substituted salicylaldimino)cobalt(II) complexes **1**. When R = CH_3, equilibrium 2 obtains

$$\text{trigonal bipyramidal dimer (high spin)} \rightleftharpoons \text{tetrahedral (high spin)} \quad (2)$$

in benzene solution[5] the nature of the associated species having been inferred from X-ray results which establish the existence of the dimer in the pure crystal.[8] When



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R = $CH_2CH_2NR'R''$ proper choice of R′ and R″ can effectuate equilibrium 3[9] in which the pentacoordinate

$$\text{octahedral monomer (high spin)} \rightleftharpoons \text{pentacoordinate monomer (high spin)} \quad (3)$$

species presumably has the approximate square-pyramidal structure determined by X-rays for the nickel and cobalt complexes having R′ = R″ = C_2H_5.[10]

Recent studies of $Co(PEt_3)_2(NCS)_2$ have established the probable existence of the equilibrium

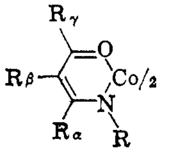
$$\text{pentacoordinate dimer (low spin)} \rightleftharpoons \text{tetrahedral (high spin)} \quad (4)$$

which constitutes the first example of an equilibrium between high- and low-spin Co(II) accompanied by a structural change.[11]

All of the above equilibria involve one or more species with an effective coordination number exceeding four. Clearly, the fundamental structural equilibrium involving strictly four-coordinate Co(II) complexes is

$$\text{planar (low spin)} \rightleftharpoons \text{tetrahedral (high spin)} \quad (5)$$

in which the two forms are interconverted by a torsional deformation proceeding in ~90° stages. This equilibrium is well established in four general classes of bischelate–nickel(II) complexes, the salicylaldimines,[12] aminotroponeimines,[13] pyrrole-2-aldimines,[14] and β-ketoamines.[15] Its occurrence in systems of complexes other than those of Ni(II) has not been previously demonstrated. We are currently engaged in a general investigation of the occurrence of the planar ⇌ tetrahedral equilibrium in quadricoordinate complexes of the divalent transition metals. The aim of this investigation is the quantitative measurement, wherever possible, of the relative stabilization of planar and tetrahedral stereoisomers of a given metal with structurally related ligands and of a series of complexes with the same ligand but different metals. In this way we hope to be able to elucidate the factors which control the preferential stabilization of one or the other stereoisomer under conditions in which either could be populated. Because of favorable solubility properties in noncoordinating solvents and as a result of the extensive characterization of the equilibrium (5) for Ni(II) complexes,[15] we have investigated a series of bis(β-ketoamino)cobalt(II) complexes (**2**). Evidence for



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the existence of equilibrium 5 is presented, and thermodynamic data characterizing the equilibrium are compared with those for the nickel complexes. Some results have already been presented in preliminary form.[16]

Experimental Section

Preparation of Ligands. Most of the α,β-unsaturated β-ketoamines were prepared as previously described.[15] Acetylacetone imide was obtained from Aldrich Chemical Co. 4-Methylamino-3-buten-2-one and 4-amino-3-methyl-3-buten-2-one were prepared by the method of Benary.[17] N,N′-Ethylenebis(4-amino-3-penten-2-one) and N,N′-ethylenebis(1-phenyl-3-amino-2-buten-1-one) were prepared according to McCarthy, *et al.*[18]

Preparation and Properties of Complexes. The Co(II) complexes listed in Table I were prepared by a modification of the nonaqueous chelation reaction previously described for the preparation of bis(β-ketoamino)nickel(II) complexes.[15] The modifications involve total exclusion of atmospheric oxygen, *necessitated by the extreme sensitivity of some of the complexes to oxidation or oxygenation*, and the use of $[(C_2H_5)_4N]_2[CoBr_4]$ as the source of metal ion. Preparation and recrystallization operations were performed using flasks and filters which were fitted with standard taper joints and vacuum stopcocks and which could be assembled and evacuated. Solutions of the complexes were exposed only to oil-pump vacuum or high-purity nitrogen. *t*-Butyl alcohol solutions of the newly formed complexes were worked up by evaporating all the solvent under vacuum and extracting the solid with hot, degassed toluene or *n*-heptane. The hot solutions were filtered; upon cooling to −15° the complexes readily crystallized. One additional recrystallization from these solvents afforded analytically pure samples as orange or reddish orange crystals. The solvents used for each complex

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Table I. Characterization of β-Ketoamino Metal(II) Complexes

R_γ	R_β	R_α	R	M	Mp, °C[a]	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
CH_3	H	CH_3	H	Co[f]	172–174	47.06	46.95	6.32	6.26	10.98	10.96
CH_3	H	CH_3	CH_3	Co[e]	169–171	50.88	50.93	7.12	7.13	9.89	9.92
CH_3	H	CH_3	CH_2^-	Co[f]	186–188[b]	51.25	51.18	6.45	6.48	9.96	9.81
CH_3	H	CH_3	n-C_3H_7	Co[e]	105–106	56.63	56.39	8.32	8.17	8.26	8.25
CH_3	H	CH_3	i-C_3H_7	Co[e,h]	170	56.63	56.86	8.32	8.28	8.26	8.17
CH_3	H	CH_3	C_6H_5	Co[f]	87–88	64.86	64.90	5.94	5.94	6.88	6.93
C_6H_5	H	CH_3	H	Co[f]	156[b]	63.32	63.58	5.31	5.57	7.39	7.51
C_6H_5	H	CH_3	CH_3	Co[f]	214–215	64.86	64.92	5.94	5.94	6.88	6.83
C_6H_5	H	CH_3	CH_2^-	Co[g,l,m]	299–300[b]	65.18	65.03	5.47	5.42	6.91	6.94
C_6H_5	H	CH_3	n-C_3H_7	Co[e]	135–136	67.37	67.64	6.96	7.20	6.04	6.18
C_6H_5	H	CH_3	i-C_3H_7	Co[f]	197–198	67.37	67.77	6.96	7.11	6.04	5.92
CF_3[c]	H	CH_3	H	Co[e,i]	89–91	33.07	33.45	2.78	2.88	7.72	7.57
CF_3[d]	H	CH_3	H	Ni[e,j]	201	33.09	32.98	2.78	2.67	7.72	7.75
CH_3	CH_3	H	H	Co[e]	157[b]	47.06	47.01	6.32	6.30	10.98	10.79
CH_3	CH_3	H	H	Ni[e,k]	225–227	47.11	47.20	6.33	6.31	10.99	10.92
CH_3	H	H	CH_3	Co[e]	99–101	47.06	46.98	6.38	6.27	10.98	10.96

[a] Uncorrected. [b] Melts with decomposition in open tube. [c] F *anal.* Calcd: 31.39. Found: 31.36. [d] F *anal.* Calcd: 31.41. Found: 31.22. [e] Extracted and recrystallized using n-heptane. [f] Extracted and recrystallized using toluene. [g] Recrystallized from acetone. [h] Pink crytals. [i] Yellow crystals. [j] Pale orange-brown crystals. [k] Gray-brown crystals. [l] Red crystals. [m] Prepared in an ethanolic solution of cobaltous acetate.

and exceptions to the above procedure are given as footnotes to Table I. Yields ranged from 30 to 70% except for the Co(II) complex with $R_\gamma = CF_3$, which was obtained in yields of ~5% in each of several attempts.

The crystalline complexes are stable in air for varying periods, the stability with respect to attack by oxygen being R = i-C_3H_7 > H > n-alkyl for given R_α and R_γ. Brown solids are formed upon exposure to air; the complexes are stable for at least 1 year when sealed *in vacuo*. In solution the stability toward oxygen attack appears to decrease in the order R = i-C_3H_7 ≫ n-alkyl > H. Complexes with R = i-C_3H_7 can be prepared in the presence of air and seem to be stable indefinitely in rigorously dry solutions,[19] whereas solutions of complexes with R = H are immediately discolored (orange → dark brown) upon contact with air. Stability toward hydrolytic decomposition appears to follow the trends observed for the nickel complexes.[15]

N,N′-Ethylenebis(4-amino-3-penten-2-ono)cobalt(II) had not been previously prepared in pure form due to its extreme oxygen sensitivity in solution.[18] The complex was obtained in well-defined crystalline form by the anaerobic, nonaqueous method. N,N′-ethylenebis(1-phenyl-3-amino-2-buten-1-ono)cobalt(II) has been reported previously[18] (mp 265° dec) but was recharacterized in the present work due to the difference in melting points of the product from the two independent preparations (*cf.* Table I).

The Ni(II) complexes were prepared by the nonaqueous method in unmodified form.[15] Bis(1-phenyl-3-amino-2-buten-1-ono)nickel(II) has been obtained previously, mp 251°;[21] present work yielded a product with mp 249–250°. Bis(4-amino-3-penten-2-ono)nickel(II) was prepared according to Hseu, *et al.*,[22] mp 248° (lit.[22] mp 247–248°).

Magnetic Susceptibility Measurements. Solutions of 0.022–0.056 *M* in complex were measured by the following two methods.

(1) **Gouy Method.** Magnetic moments of complexes in the solid and solution phases at room temperature were obtained as previously described.[15] In solution measurements extreme care was taken to exclude rigorously moisture and oxygen. Solvents were freshly distilled from P_2O_5 in a stream of dry, high-purity nitrogen and then introduced into evacuated Gouy tubes which were attached to the distilling apparatus and which contained weighed amounts of sample. The tubes were immediately sealed, and the measurements were performed within 10 min. Measurements of chloroform solutions containing 15% v/v tetramethylsilane were carried out for comparison with susceptibilities obtained by the nmr method.

(2) **Nmr Method.** The procedure due to Evans[23] was used to obtain magnetic data over a range of temperatures. A Varian A-60 spectrometer equipped with a variable-temperature probe was employed, and the temperature calibration at each point was monitored by measuring the signal separations of methanol or ethylene glycol. Solutions were prepared under nitrogen and transferred to sample tubes by means of syringes with careful exclusion of air and moisture. The sample tubes contained a sealed capillary of pure solvent consisting of ~15% v/v (~7% w/w) of tetramethylsilane in chloroform. Solutions were prepared using this same solvent. The separation of the TMS signals (solution–solvent) was measured in each case, because it was found that measurement of chloroform signals gave moments considerably higher than those obtained by the Gouy method on identical solutions at the same temperature. For example, measurement of the moment of bis(1-phenyl-3-isopropylamino-2-buten-1-ono)cobalt(II) gave 4.72 BM using chloroform signals, 4.43 BM using TMS signals, and 4.37 BM by the Gouy method. The excessive upfield shifts leading to erroneously large magnetic moments are believed due to a pseudo-contact shift[24] produced by the g value anisotropy of the complexes and the slight tendency of polar solvent molecules to associate with them. These results clearly point out that the measured frequency separations used to calculate magnetic moments[23] should be due solely to bulk susceptibility differences and contain no contributions from isotropic contact shifts. Temperature dependences of moments of the complexes with R = H were found to be completely *reversible* over a range of ~100°. However, when the solutions were heated above 60–70°, the measured moments appeared too large, and the moments at lower temperatures could not be satisfactorily reproduced upon cycling the temperatures. These effects are attributed to hydrolysis of the complexes brought about by traces of moisture in the TMS, which was apparently not rigorously dried by storage over molecular sieves. Magnetic data set out in Table IV were obtained from measurement of a single solution of each complex and correspond to the plots of Figure 5. In determining thermodynamic quantities, at least two independent solutions of each complex were measured and the data evaluated by least squares.

Spectral Measurements. Measurements of electronic spectra were obtained using a Cary Model 14 spectrophotometer. Solutions of complexes susceptible to attack by oxygen were prepared in the absence of oxygen and moisture using a quartz cell equipped

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(19) Similar stability toward oxygen has been observed for solutions of bis(N-R-salicylaldimino)cobalt(II) complexes in which R = α-branched alkyl group.[7,12e] This effect may be due to the steric destabilization of the tris complex, a probable oxidation product,[20] with respect to the bis complex affected by the bulky nature of the R groups.

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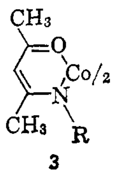
with a vacuum stopcock. Solution temperatures were controlled to ±1° using a thermostated cell compartment.

Results and Discussion

Bis(β-ketoamino)cobalt(II) complexes synthesized in this work are listed in Table I. The majority of the complexes are derived from the condensation products of acetylacetone or benzoylacetone with primary amines and have structures **3** and **4**. As suggested earlier,[25] these complexes are abbreviated Co(R-AA)$_2$ and Co(R-BA)$_2$, respectively. Bis(β-ketoamino)cobalt(II) complexes have not been previously prepared except for bis(1-phenyl-3-hydroxyamino-2-propen-1-ono)cobalt(II)[21] and several complexes of type **3** with R = aryl which have been briefly reported in an abstract.[26] A few tetradentate β-ketoamino Co(II) complexes have already been prepared.[18,27] Those of interest in the present work have the structure **5** and are designated as Co(AA)$_2$(en) ($R_\gamma = CH_3$) or Co(BA)$_2$(en) ($R_\gamma = C_6H_5$). These complexes are assumed to have an essentially planar structure.



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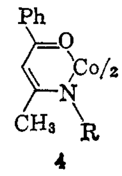

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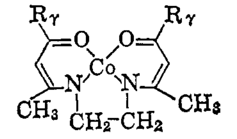

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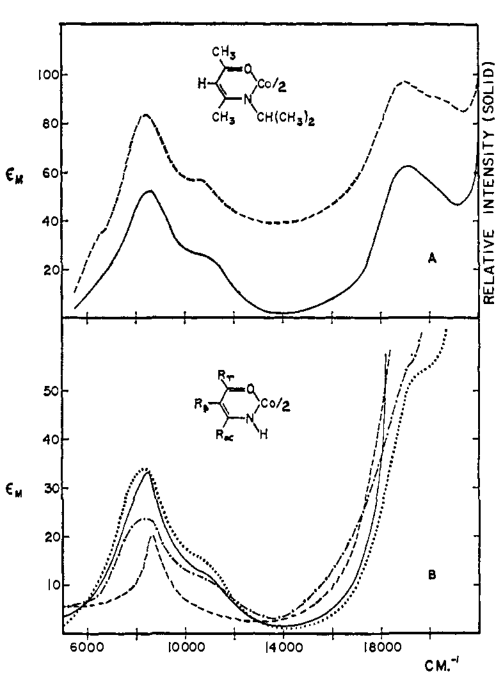

Figure 1. (A) Ligand field spectrum of bis(4-isopropylamino-3-penten-2-ono)Co(II): – – – –, hydrocarbon mull; ———, chloroform solution. (B) Ligand field spectra in chloroform solution at 25°: . . . ., $R_\gamma = R_\alpha = CH_3, R_\beta = H$; ———, $R_\gamma = C_6H_5, R_\alpha = CH_3, R_\beta = H$; — · —, $R_\gamma = CF_3, R\alpha = CH_3, R_\beta = H$; – – – –, $R_\gamma = R_\beta = CH_3, R_\alpha = H$.

On the basis of magnetic and spectral behavior, the bis(β-ketoamino)Co(II) complexes may be divided into two groups, defined by the nature of the nitrogen substituent. I: $R_\alpha = R_\gamma = CH_3$, $R_\beta = H$, $R = CH_3$, n-C_3H_7, i-C_3H_7, C_6H_5; $R_\alpha = CH_3$, $R_\beta = H$, $R_\gamma = C_6H_5$, $R = CH_3$, n-C_3H_7, i-C_3H_7; $R_\alpha = R_\beta = H$, $R_\gamma = CH_3$, $R = CH_3$; and II: $R_\alpha = R_\gamma = CH_3$, $R_\beta = H$, $R = H$; $R_\alpha = CH_3$, $R_\beta = H$, $R_\gamma = C_6H_5$, $R = H$; $R_\alpha = H$, $R_\beta = R_\gamma = CH_3$, $R = H$. Magnetic and spectral data for complexes of both groups are set out in Tables II, III, and IV. For the purpose of establishing structures the interpretation of these data for group I complexes is straightforward. All of these complexes have moments in the range 4.22–4.44 BM in the solid and 4.28–4.50 BM in solutions of noncoordinating solvents. Further, the ligand field spectra are essentially identical in the solid and in solution and consist of a maximum at ~8400 cm^{-1}, a shoulder very prominent in all cases at ~10,500 cm^{-1}, and a further maximum in the visible range. The first two features are assigned as components of $\nu_2[^4A_2 \rightarrow {}^4T_1]$ and the third as $\nu_3[^4A_2 \rightarrow {}^4T_1(P)]$ in idealized tetrahedral symmetry. Spectra of the representative complex Co(i-Pr-AA)$_2$ are shown in Figure 1. These spectral and magnetic properties are convincingly similar to those of the salicylaldimine complexes **1** with R = alkyl[6,7,20b,28] and aryl,[28–30] which may be satisfactorily interpreted on the basis of a pseudo-tetrahedral structure. In addition, several of these complexes have been shown by X-ray results[31] to possess a gross tetrahedral configuration, and the solution dipole moments of the complexes are consistent with this configuration in nondonor solvents.[32] It might be argued that the intensities of the ligand field bands (*cf.* Table III) are anomalously low for tetrahedral Co(II). Indeed, this appears to be the case. However, comparison of these spectra with the solid and solution phase spectra of bis(dipivaloylmethanato)cobalt(II),[3b] which is known to have a somewhat distorted tetrahedral structure in the solid,[33] reveals a striking similarity in band positions and intensities. The origin of the low intensities in terms of distortions from strict tetrahedral symmetry has been discussed elsewhere[33] and may be applicable in some degree to the β-ketoamine complexes, although it is obvious that the ligand fields in these complexes must of necessity be of

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[30] B. O. West, *J. Chem. Soc.*, 1374 (1962).

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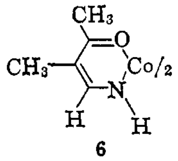
[32] M. Ciampolini, F. Maggio, and F. P. Cavasino, *Inorg. Chem.*, **3**, 1188 (1964).

[33] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **84**, 872 (1962); F. A. Cotton and J. S. Wood, *Inorg. Chem.*, **3**, 245 (1964).

Table II. Magnetic Moments in Solid and Solution Phases of β-Ketoaminocobalt(II) Complexes[a]

R_γ	R_β	R_α	R	Solid, μ_{eff}, BM	Solution: Solvent	Solution: μ_{eff}, BM
CH_3	H	CH_3	H	2.23	$CHCl_3$	3.86
					CH_2Cl_2	3.75
					$CHCl_3$–TMS[c]	4.09
CH_3	H	CH_3	CH_3	4.22	Toluene	4.36
CH_3	H	CH_3	CH_2^-	2.23	$CHCl_3$	2.13[f]
CH_3	H	CH_3	n-C_3H_7	4.44	$CHCl_3$	4.39
CH_3	H	CH_3	i-C_3H_7	4.35	$CHCl_3$	4.42
					Toluene	4.50
CH_3	H	CH_3	C_6H_5	4.35	$CHCl_3$	4.42[b]
C_6H_5	H	CH_3	H	2.33	$CHCl_3$	3.30
					CH_2Cl_2	3.26
					Toluene	3.22
					$CHCl_3$–TMS[c]	3.64
					$CHCl_3$–C_2H_5OH[e]	4.15
C_6H_5	H	CH_3	CH_3	4.30	$CHCl_3$	4.36
C_6H_5	H	CH_3	CH_2^-	2.33	...	d
C_6H_5	H	CH_3	n-C_3H_7	4.39	CCl_4	4.35[b]
C_6H_5	H	CH_3	i-C_3H_7	4.30	$CHCl_3$	4.37
					Toluene	4.38
CH_3	CH_3	H	H	2.17	$CHCl_3$	2.70
					$CHCl_3$–TMS[c]	2 84
CH_3	H	H	CH_3	4.37	$CHCl_3$	4.28

[a] All moments calculated from the Curie law and measured at ambient room temperature (20–26°) by the Gouy method unless otherwise indicated. [b] Measured by nmr method. [c] 15% v/v tetramethylsilane in chloroform. [d] Insufficiently soluble for accurate measurement. [e] 15% w/w ethanol in chloroform. [f] Value may be slightly low due to oxidation; see Figure 2 and footnote b of Table III.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lower symmetry than that in a structurally similar β-diketone complex. It may be concluded with certainty that all group I complexes possess a gross tetrahedral configuration in both the crystalline and solution phases. The degree of tetrahedrality can be established only by X-ray structural determination.

In contrast to group I complexes, the three group II complexes, Co(H-AA)$_2$, Co(H-BA)$_2$, and **6**, are low spin in their pure crystalline phases (2.17–2.33 BM), as is bis(1-phenyl-3-hydroxyamino-2-propen-1-ono)cobalt (II) (2.21 BM[21]). Moments of 2.2–2.9 BM are considered characteristic of low-spin four-coordinate Co(II),[34] a number of which (such as **5**) are constrained by ligand structure to have an essentially planar structure. Additionally, the crystalline group II complexes display an absorption feature at ~8500 cm^{-1}, which is nearly identical in contour and energy with the band displayed by Co(AA)$_2$(en) and Co(BA)$_2$(en)[35] (compare Figures 2 and 3). The intensity of this band indicates that it is a ligand field transition, but because of the present uncertainty in the ground-state electronic configurations of low spin **2** and **5**, the transition involved has not yet been assigned. However, inasmuch as a similar feature appears at 8300–8500 cm^{-1} in the tetradentate salicylaldimine analogs[36] of **5**, this band is characteristic of low-spin planar Co(II).

Identification of the Solution Equilibrium of R = H Complexes. It is clearly evident that group II complexes, upon dissolution in noncoordinating solvents, do not completely retain their low-spin planar configurations. In chloroform, for example, the spectra in the 6000–11,000-cm^{-1} region (*cf.* Figure 1) are distinctly different in all but one case (**6**) from the spectra of the tetradentate complexes **5** (Figure 2). (The

Table III. Spectral Data for β-Ketoaminocobalt(II) Complexes in the 20,400–4600-Cm^{-1} Range

R_γ	R_β	R_α	R	Medium	λ_{max}, cm^{-1} (ϵ_m)[a]				
CH_3	H	CH_3	H	$CHCl_3$	19600 (~40)[c]		10400 (sh)	8400 (36)	~7700 (sh)
				Mull	18700 (sh)		8900 (sh)	8400	6200–4600[d]
CH_3	H	CH_3	CH_3	Toluene	20400 (~50)[c]		10800 (sh)	8260 (52)	
CH_3	H	CH_3	n-C_3H_7	Mull		16200	10500 (sh)	8400	
CH_3	H	CH_3	i-C_3H_7	$CHCl_3$	20400 (sh)	19100 (63)	10500 (sh)	8460 (52)	~6700 (sh)
				Mull	20400 (sh)	19000	10500 (sh)	8400	~6700 (sh)
CH_3	H	CH_3	C_6H_5	$CHCl_3$		19200 (sh)	10500 (sh)	8140 (70)	
				Mull		15700 (sh)	10500 (sh)	8340	~6700 (sh)
C_6H_5	H	CH_3	H	$CHCl_3$			10400 (sh)	8460 (33)	~7600 (sh)
				Mull	18700 (sh)		9100 (sh)	8460	6200–4600[d]
C_6H_5	H	CH_3	i-C_3H_7	$CHCl_3$		17900 (sh)	10500 (sh)	8460 (62)	~6700 (sh)
				Mull		16200 (sh)	10600 (sh)	8550	~6700 (sh)
CF_3	H	CH_3	H	$CHCl_3$	19000 (sh)		10400 (sh)	8500 (24)	7700 (sh)
CH_3	CH_3	H	H	$CHCl_3$				8620 (20)	7600 (sh)
				Mull			8800 (sh)	8550	6200–5000[d]
CH_3	H	CH_3	CH_2^-	$CHCl_3$		14600 (6)[b]		8580 (14)	6200–4600[d]
				Mull				8500	6200–4600[d]
C_6H_5	H	CH_3	CH_2^-	$CHCl_3$		15100 (sh)[b]		8600 (16)	6200–4600[d]
				Mull				8550	6200–4600[d]

[a] sh = shoulder. [b] Due to small amount of oxidized complex which persisted despite rigorous precautions to exclude oxygen. [c] Uncertainty in ϵ_m is due to uncertainty of contribution of underlying intensity for overlapping bands. [d] Continuous irregular absorption in this region.

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(34) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 192 (1965).

(35) The electronic properties of these *cis*-planar complexes are taken as essentially identical with those manifested by the *trans*-planar forms of the group II complexes. This relation is valid only if the rule of average ligand field environment holds. Paramagnetic resonance studies of *trans*-planar bis(salicylaldimino)Cu(II), which, because of its electronic configuration, should be sensitive to in-plane anisotropy, show that the *g* factor is nearly the same in the Cu–N and Cu–O directions (A. H. Maki and B. R. McGarvey, *J. Chem. Phys.*, **29**, 35 (1958)), thereby providing support that a planar N_2O_2 coordination sphere, such as is present in **2** and **5**, provides an effectively isotropic environment.

(36) H. Nishikawa and S. Yamada, *Bull. Chem. Soc. Japan*, **37**, 8 (1964).

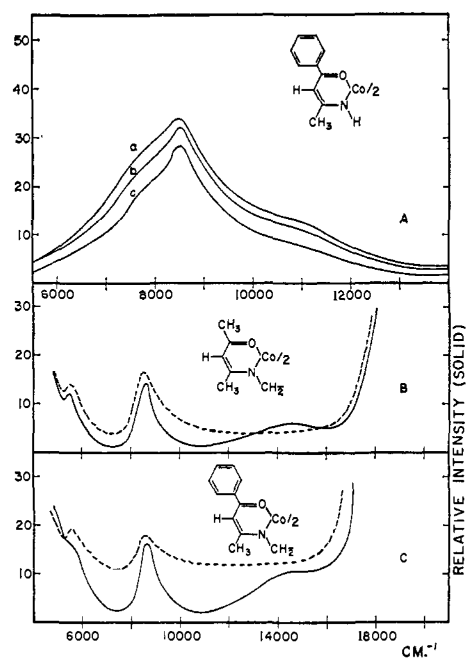


Figure 2. (A) Spectrum of bis(1-phenyl-3-amino-2-buten-1-ono)-Co(II) in chloroform: a, 60°; b, 0°; c, −30°. (B) Spectrum of N,N′-ethylenebis(4-amino-3-penten-2-ono)Co(II): - - - -, hydrocarbon mull; ———, chloroform solution. (C) Spectrum of N,N′-ethylenebis(1-phenyl-3-amino-2-buten-1-ono)Co(II): - - - -, hydrocarbon mull; ———, chloroform solution.

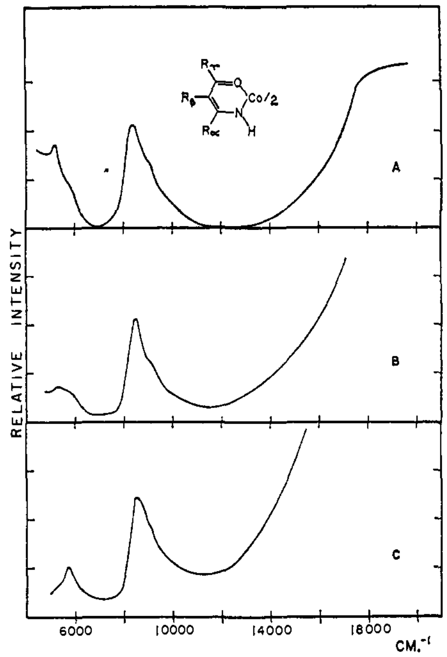
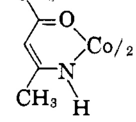
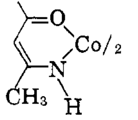
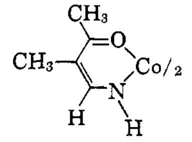


Figure 3. Spectra of bis(β-ketoamino)Co(II) complexes in hydrocarbon mulls: (A) $R_\gamma = R_\alpha = CH_3, R_\beta = H$; (B) $R_\gamma = C_6H_5, R_\alpha = CH_3, R_\beta = H$; (C) $R_\gamma = R_\beta = CH_3, R_\alpha = H$.

solubility of $Co(AA)_2(en)$ permitted a magnetic measurement in solution, which showed that the complex retains its doublet ground state.) The maximum and shoulder of ν_2 of the tetrahedral form are particularly evident, and the intensities are markedly reduced compared to the wholly tetrahedral complexes. The situation is somewhat complicated because of the fact that both the low-spin and high-spin forms possess an absorption band at ~8500 cm⁻¹. The band envelopes are, however, observably different, the low-spin form possessing a characteristically narrow band (~1100 cm⁻¹ half-width) whereas the high-spin form exhibits a broader feature at this energy and the clearly defined shoulder at 10,500 cm⁻¹.

Table IV. Temperature Dependence of Magnetic Moments and Free-Energy Changes for the Planar ⇌ Tetrahedral Equilibrium[a]

								
Temp, °K	μ_{eff},[b] BM	ΔF,[c] cal/mole	Temp, °K	μ_{eff},[b] BM	ΔF,[c] cal/mole	Temp, °K	μ_{eff},[b] BM	ΔF,[c] cal/mole
237	3.86	−396	228	3.26	256	239	2.55	929
246	3.86	−411	245	3.36	145	242	2.58	895
251	3.86	−419	263	3.47	40	248	2.60	888
265	3.89	−484	281	3.56	−60	263	2.68	826
284	3.94	−598	299	3.64	−164	275	2.74	780
301	3.96	−669	324	3.75	−336	289	2.80	739
325	3.99	−782	343[d]	3.86	−541	300	2.88	662
345	4.00	−852				308	2.90	654
364[d]	4.08	−1100				312[d]	2.96	586

[a] Measurements by nmr method in ~15% v/v TMS–$CHCl_3$. [b] Error estimated to be ±2%. [c] Error estimated to be ±18% assuming no error in the limiting values of μ_p and μ_t. [d] Values of ΔF at these temperatures show deviation from the linear ΔF *vs.* T relationship observed at lower temperatures, probably due to hydrolytic decomposition (see the Experimental Section).

The magnetic data of Table IV reveal solution magnetic moments per cobalt intermediate between high- and low-spin values, as inferred from the data of Table II. It is seen that, in a qualitative fashion, the moments increase as do the intensities of the ν_2 components in Figure 1. The complex with $R_\gamma = CF_3$, $R_\alpha = CH_3$, $R_\beta = H$ could be obtained in low yields only and was not subjected to magnetic studies.

The preceding data are highly suggestive of an equilibrium involving high-spin tetrahedral Co(II) and a low-spin form. To establish the nature of this equilibrium, we first eliminate equilibria 1–4 which have been reported in solutions of other Co(II) complexes. Equilibria 1, 2, and 3 can be discounted immediately since they implicate only high-spin forms. Indeed, (3) cannot apply because no R group in the present study is functionally substituted. This leaves (4) or some variant thereof in which the polymeric form is low spin. Direct molecular weight determinations by osmometry were not possible owing to the extreme sensitivity of the solutions to oxygen. To ascertain the existence of associated species, Beer's law studies of the three group II complexes were performed at two wavelengths in the concentration range 0.005–0.040 *M*, which overlaps with that used in the magnetic and all other spectral measurements. As is observed in Figure 4 an excellent Beer's law dependence obtains in all three cases. The solution chemistry of bis(salicylaldimino)nickel(II) complexes and, to a very much smaller extent, of bis(β-ketoamino)nickel(II) complexes, is complicated by associative equilibria in which the metal ion in the oligomer has a coordination number exceeding four which is produced by axial interaction with donor oxygens of other

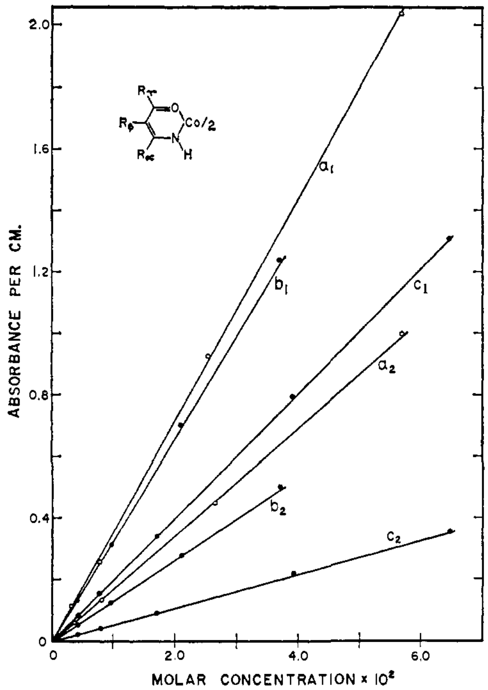


Figure 4. Beer's law studies of bis(β-ketoamino)Co(II) complexes in chloroform solution at 25°: (a) $R_\gamma = R_\alpha = CH_3$, $R_\beta = H$; (b) $R_\gamma = C_6H_5$, $R_\alpha = CH_3$, $R_\beta = H$; (c) $R_\gamma = R_\beta = CH_3$, $R_\alpha = H$; a_1 at 8400 cm^{-1}, b_1 at 8470 cm^{-1}, c_1 at 8620 cm^{-1}; a_2, b_2, c_2 at 10,400 cm^{-1}.

molecules.[25] As further insurance against the presence of associated low-spin species, an attempt was made to simulate the coordination sphere of Co(II) in an oligomer. The magnetic moment of Co(H-BA)$_2$ *increased* upon the addition of ethanol to a chloroform solution (*cf.* Table II), strongly suggesting that any polymerization process involving intermolecular Co···O interactions would produce high-spin rather than low-spin oligomers. A similar situation occurs when the complexes **1** are dissolved in pyridine.[28,30] Finally, the solution spectra of the group II complexes in Figure 1 bear no convincing resemblance to the five-coordinate bis(salicylaldimino)cobalt(II) monopyridinate[37] or to the five- and six-coordinate monomer and dimer, respectively, of cyclohexylamine–bis(acetylacetonato)cobalt(II) which have been prepared recently.[38]

We have also investigated the occurrence of another equilibrium seemingly ruled out by the Beer's law results but for which there is some precedent. Tetradentate (but not bisbidentate) salicylaldiminecobalt(II) complexes are known to absorb oxygen reversibly in an equilibrium reaction,[39] which in the more well-defined cases may be represented by

$$2 \text{ planar (low spin)} + O_2 \rightleftharpoons 2 \text{ planar}\cdot O_2 \text{ (diamagnetic)} \quad (6)$$

In the present systems this reaction might be reformulated as

$$2 \text{ tetrahedral (high spin)} + O_2 \rightleftharpoons 2 \text{ planar}\cdot O_2 \text{ (diamagnetic or } \mu < 4.3 \text{ BM/Co)} \quad (7)$$

In order to discount this equilibrium, or any equilibrium involving oxygen, the following experiment was performed. Co(H-BA)$_2$ solid was evacuated at 25° for 20 hr to remove any traces of residual oxygen,[40] and then solutions for Gouy magnetic measurements were prepared as described in the Experimental Section except that the operations were performed under nitrogen exhaustively freed of oxygen by the following treatment. The commercial prepurified gas was passed through a heated tower (6 × 35 cm) of hydrogen-reduced cuprous oxide deposited on kieselguhr and maintained at 180°, chromous chloride solution, and then dried by passage through sulfuric acid, solid potassium hydroxide, and phosphorus pentoxide. Measurements of these solutions yielded moments within ±0.05 BM of those obtained on solutions prepared with very careful but less rigorous exclusion of oxygen. It is concluded that oxygen does not play a significant role in determining solute composition and that equilibria such as (7) may be eliminated.

It is concluded that all data and observations are consistent only with the configurational equilibrium 5 which we further specify as

$$\text{planar } (S = 1/2, \sim 2.2 \text{ BM}) \rightleftharpoons \text{tetrahedral } (S = 3/2, \sim 4.4 \text{ BM}) \quad (8)$$

This equilibrium is to be carefully distinguished from that of certain octahedral Co(II) complexes[41] whose doublet and quartet states are thermally occupied without necessitating any gross structural change.

Thermodynamics of the Configurational Equilibrium. The endothermic nature of equilibrium 8 is demonstrated by the temperature dependence of the spectral and magnetic properties. In Figure 2 it is observed that the over-all band width and intensity of the near-infrared absorption band increases with increasing temperature, as does the intensity of the shoulder characteristic of the tetrahedral form. The magnetic data as a function of temperature are shown in Table IV and indicate that (8) is displaced to the right as the temperature is raised.[42]

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(37) S. Yamada and H. Nishikawa, *Bull. Chem. Soc. Japan*, **38**, 683 (1965).

(38) J. A. Bertrand, F. A. Cotton, and W. J. Hart, *Inorg. Chem.*, **3**, 1007 (1964), and references therein.

(39) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp 337–352; L. H. Vogt, Jr., H. M. Faigenbaum, and S. E. Wiberley, *Chem. Rev.*, **63**, 269 (1963).

(40) Note that the elemental analyses in Table I preclude the existence of appreciable, consistent amounts of molecular oxygen in the crystalline solids. All physical measurements were performed on analyzed samples.

(41) R. C. Stoufer, D. H. Busch, and W. B. Hadley, *J. Am. Chem. Soc.*, **83**, 3733 (1961).

(42) In this connection the question of the contribution to these trends of the intrinsic temperature dependence of the magnetic moments of the high- and low-spin forms might be raised. In the cases of Co(H-AA)$_2$ and Co(H-BA)$_2$ the ν_2 features are readily observable over the temperature range used in the magnetic studies, thus proving that the tetrahedral form is present. Magnetic measurements of the electronically similar tetrahedral salicylaldimine complexes in the pure crystalline state from 80 to 300°K show that the Curie–Weiss law is obeyed but that θ is very small (<5°).[28,30] Thus the Curie moments vary by no more than 1% from room temperature values over this range. It is readily shown[43] and always observed[28,30,34] that tetrahedral (or pseudotetrahedral) Co(II) complexes possess moments *exceeding* the spin-only value. Measurements of the completely tetrahedral complexes Co(*i*-Pr-AA)$_2$ and Co(*i*-Pr-BA)$_2$ in solution over a temperature range yielded no moments lower than 4.2 BM. It follows that moments per cobalt less than this value must be attributed to the presence of the low-spin form. The temperature dependence of the magnetically dilute low-spin form is less readily assessed. Several tetradentate salicylaldimine Co(II) complexes have been studied in the pure solid over a temperature range.[34] Not all obey the Curie–Weiss law but those which do have θ values of 7–52°. It is not known if these effects are due to lack of magnetic dilution, perhaps accompanied in the non-Curie–Weiss cases by phase changes, or to an intrinsic temperature dependence of the moments. For Co(AA)$_2$(en) the difference of 0.1 BM between solid and solution moments indicates that the solid is essentially magnetically dilute. Because the moment of **6** is ~0.6 BM higher at room temperature in solution and does not decrease below 2.55 BM at the lowest temperature of measurement, it is concluded that the increments of moment

Defining the equilibrium constant for (8) as $K = N_t/N_p$, where N_t and N_p are the mole fractions of the tetrahedral and planar forms, respectively, and using $\Delta F = -RT \ln K$ and $N_t + N_p = 1$, it is readily shown that

$$N_p = (1 + e^{-\Delta F/RT})^{-1} \text{ and } N_t = (1 + e^{\Delta F/RT})^{-1} \quad (9)$$

Taking the corrected molar susceptibilities per cobalt of the equilibrium mixture, the planar form, and the tetrahedral form as $\chi^M{}_{obsd}$, $\chi^M{}_p$, and $\chi^M{}_t$, it follows that

$$\chi^M{}_{obsd} = N_t\chi^M{}_t + N_p\chi^M{}_p \quad (10)$$

from which is obtained

$$\Delta F = RT \ln \frac{\chi^M{}_t - \chi^M{}_{obsd}}{\chi^M{}_{obsd} - \chi^M{}_p} = RT \ln \frac{\mu^2{}_t - \mu^2{}_{obsd}}{\mu^2{}_{obsd} - \mu^2{}_p} \quad (11)$$

The values of μ are the magnetic moments calculated from the Curie law, $\mu = 2.84\,(\chi^M T)^{1/2}$. In the evaulation of the free-energy changes, μ_t was taken as 4.38 BM, and the moments of the low-spin, crystalline complexes were used for μ_p. Several different determinations for each complex of the temperature dependence of the magnetic moment were carried out. Measurements were made by the nmr method and were checked at room temperature against the moments obtained by the Gouy method using an identical solution. In the three cases the agreement is ±0.13 BM or less (compare Tables II and IV). It is noteworthy that in the mixed solvents the moments are always higher than in pure chloroform; the addition of TMS displaces the equilibrium toward the tetrahedral form. Results of different temperature runs for each complex were in satisfactory agreement. Shown in Table IV and Figure 5 are results derived from a typical run for each complex. The $\Delta F^{298°}$, ΔH, and ΔS values in Table V were obtained by taking data from all runs and applying a least-mean-squares fit of the ΔF values calculated from eq 11 *vs.* temperature. The satisfactory linearity of the calculated free energy with temperature as required by $\Delta F = \Delta H - T\Delta S$ is further indication of the existence of a single equilibrium over the temperature range studied.

The mole fractions of tetrahedral form are readily calculated from the derived least-mean-squares free-energy function. The results at 25° are given in Table V. To verify further the existence of the configurational equilibrium and the validity of the thermodynamic data, values of N_t were obtained by an independent method based on spectral intensities in the 6000–12,000-cm^{-1} region at 25°. For the complexes Co(H-AA)$_2$ and Co(H-BA)$_2$ the integrated intensities of the ν_2 feature in the limit of $N_t = 1$ were taken as those observed for Co(*i*-Pr-AA)$_2$ and Co(*i*-Pr-BA)$_2$ in the same solvent. Likewise, the integrated intensities of the ~8500-cm^{-1} bands in the limit $N_p = 1$ were assumed to be those of Co(AA)$_2$(en) and Co(BA)$_2$(en), respectively. The integrated intensities of the standards and the equilibrium mixtures were determined by direct weighing of the appropriately cut experimental spectral traces followed by normalization of the areas so obtained to fixed concentration and path length. The mole fraction of tetrahedral species is then given by

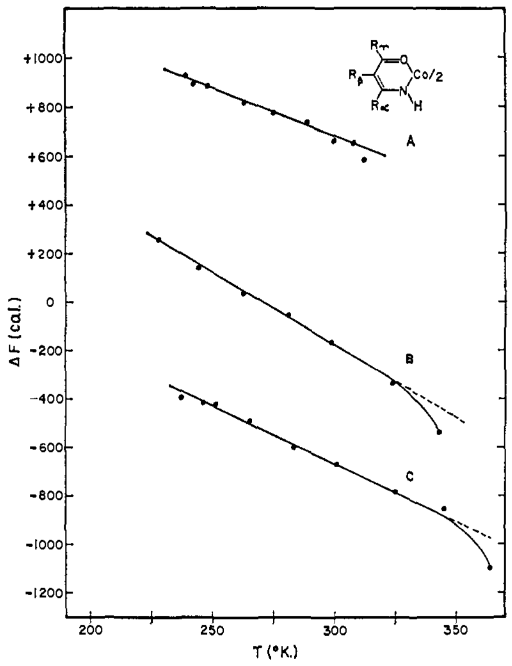

Figure 5. Temperature dependence of free-energy change for the planar-tetrahedral conversion of bis(β-ketoamino)Co(II) complexes in 15% (v/v) TMS/CHCl$_3$ solution: (A) $R_\gamma = R_\beta = CH_3$, $R_\alpha = H$; (B) $R_\gamma = C_6H_5$, $R_\alpha = CH_3$, $R_\beta = H$; (C) $R_\gamma = R_\alpha = CH_3$, $R_\beta = H$.

$$N_t = \frac{A_{obsd} - A_p}{A_t - A_p} \quad (12)$$

in which A represents the normalized areas. The same procedure was carried out for **6** using as standards Co(*i*-Pr-AA)$_2$ and Co(AA)$_2$(en). Results for the three group II complexes are set out in Table V. Agreement between the N_t values obtained from magnetic and spectral data is concluded to be highly satisfactory.

Structural Effects on the Configurational Equilibrium and Comparison with Ni(II) Complexes. The critical structural feature which distinguishes the complexes of groups I and II is the nitrogen substituent R. In all cases thus far examined, complexes with R groups methyl or larger are completely tetrahedral in both solid and solution, whereas those with R = H are planar in the solid and are involved in the configurational equilibrium 8 in solution. The implication is that a torsional distortion induced by steric interaction in the (assumed) *trans*-planar form destabilizes this stereoisomer. When R = H, however, the degree of steric interaction is very much less or absent such that both stereoisomers are populated in solution at ordinary temperatures. In these cases electronic effects may be of equal or much greater importance than steric forces, as judged by the marked dependence of equilibrium position on R_α, R_β, and R_γ, the variation of which with R = H is not expected to produce marked steric changes in either stereoisomer. Enthalpy changes reflect the

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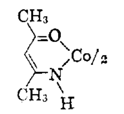
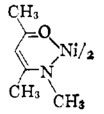
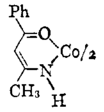
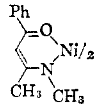
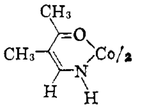
above ~2.2 BM arise from the presence of the tetrahedral form. This isomer could not be directly detected by spectral measurements; no features clearly due to ν_2 were recognizable in chloroform solution up to 60°. (Using the free-energy function given in Table V, N_t is calculated at 60° to be 0.31, a value which may be too low to allow clear detection of ν_2 even though the tetrahedral form is present.) In the following analysis of the temperature dependence of the solution magnetic moments, it is assumed that displacement of equilibrium 8 is solely responsible for the change in moments with temperature. A definite, but at present indeterminate, contribution from an intrinsic temperature dependence of the low-spin moments cannot be altogether ruled out, however.

(43) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, 31, 788 (1959).

Table V. Comparison of Thermodynamic Data for Planar ⇌ Tetrahedral Equilibria of Co(II) and Ni(II) Complexes in Chloroform Solution

Complex	Temp range, °K[a]	ΔH[b], cal/mole	ΔS,[b] eu	ΔS–ΔS_{elec},[c] eu	$\Delta F^{298°}$, cal/mole	$N_t^{298°}$
	240–345	706 ± 60	4.62 ± 0.50	3.24	−671 ± 100	0.76 (magnetic) 0.66 (spectral)
	230–350	2950 ± 10	3.98 ± 0.20	1.80	1770 ± 70	0.048
	230–330	1640 ± 60	5.96 ± 0.60	4.58	−136 ± 100	0.56 (magnetic) 0.46 (spectral)
	240–360	4810 ± 10	8.22 ± 0.20	6.04	2360 ± 70	0.018
	240–310	1910 ± 150	4.15 ± 0.70	2.77	673 ± 120	0.24 (magnetic) 0.20 (spectral)

[a] Range over which ΔF values calculated from magnetic moments or contact shifts vary linearly with temperature. [b] Estimated errors refer to temperature range of measurement. [c] ΔS_{elec} (Ni) = $R \ln 3$ = 2.18 eu, ΔS_{elec} (Co) = $R \ln 2$ = 1.38 eu.

effects of these substituents, while entropy changes show the expected much smaller variation. The electronic entropy change $R \ln 2 = 1.38$ eu is a constant contribution to all ΔS values, the variation of which is believed to be due principally to different degrees of solvation of the two stereoisomers.

A detailed comparison of thermodynamic data for Ni(II) and Co(II) complexes involved in equilibrium 8 will be deferred until a later communication which will present a larger body of results and a more complete analysis. However, some limited comparisons are in order at present. Ni(H-AA)$_2$, Ni(H-BA)$_2$, and the Ni(II) analog of **6** exhibit no proton contact shifts up to 80° in chloroform solution. Because less than 1% tetrahedral form can be detected by the contact shift technique, we conclude that at 80° $N_t < 0.01$ and $\Delta F > 3200$ cal/mole for these four complexes. Alteration of the R group from H to CH$_3$ produces small but measurable amounts of tetrahedral form of the two complexes studied, Ni(Me-AA)$_2$ and Ni(Me-BA)$_2$. The thermodynamic values characterizing the structural change of the two complexes were obtained as previously described[15] using the relation[44]

$$\frac{\Delta f_i}{f} = -a_i\left(\frac{\gamma_e}{\gamma_H}\right)\frac{g\beta S(S+1)}{6SKT}[e^{\Delta F/RT}+1]^{-1} \qquad (13)$$

in which the symbols have their usual meanings.[15] Plots of ΔF *vs.* T are linear over the temperature range of measurement; the results are set out in Table V. On the basis of these and earlier[15] results, we draw the following conclusions, *which apply specifically to β-ketoamine complexes in chloroform solution* but to which there appear to be no known exceptions with other ligand systems. (i) Ligands which stabilize a measurable amount of tetrahedral Ni(II) induce ~100% tetrahedral Co(II). (ii) Ligands which stabilize a measurable amount of planar Co(II) induce ~100% planar Ni(II). The converses of these statements are not true. From these statements it follows that stabilization of measurable amounts of planar and tetrahedral forms of *both* Co(II) and Ni(II) has not yet been effected by a given ligand system. That with R = H gives planar and tetrahedral Co(II) but only planar Ni(II), whereas that with R = CH$_3$ yields planar and tetrahedral Ni(II) but only tetrahedral Co(II). Accordingly, comparison of thermodynamic data for Ni(II) and Co(II) complexes is made using ligand systems as closely structurally related as possible. For this purpose the pairs Ni(Me-AA)$_2$–Co(H-AA)$_2$ and Ni(Me-BA)$_2$–Co(H-BA)$_2$ are compared in that order. The limited data permit the following tentative conclusions at 298°K (the ΔΔ symbol indicates the difference between Ni(II) and Co(II) complexes). (iii) The relative equilibrium positions are due mainly, though not overwhelmingly, to the difference in enthalpy changes, $\Delta\Delta H$ ($T\Delta\Delta S$ values amount to 8 and 27% of $\Delta\Delta F$ values for the pairs). (iv) $\Delta\Delta S$ values, after correction for constant entropy contributions arising from changes in ground-state spin multiplicities, fall in the narrow range of ±1.5 eu; these values are ascribed principally to differences in solvation of the stereoisomers, an effect which does not appear to depend strongly on whether R = CH$_3$ or H. (v) $\Delta\Delta H$ values are not independent of ligand structure (at least for the above two pairs), the values being 2240 and 3270 cal/mole. Statement v implies that the relative stabilization of planar and tetrahedral forms in the pairs above is not due entirely to differences in electronic energies (most simply crystal field stabilization energies)

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(44) W. DeW. Horrocks, *J. Am. Chem. Soc.*, 87, 3779 (1965). Note that in order to compare ΔF and ΔS data in ref 15 with those in Table V, ΔF values in ref 15 should be decreased by $RT \ln 3$ and the accompanying ΔS values increased by $R \ln 3$.

of the stereoisomers but depends in part on other enthalpy changes which do not completely cancel when computing and comparing $\Delta\Delta H$ values. A further and detailed analysis of $\Delta\Delta H$ values for these and other pairs of Ni(II) and Co(II) complexes will be presented when additional data are obtained.

Although the relative stabilization of the planar and tetrahedral forms of Ni(II) and Co(II) with related ligands cannot yet be analyzed in detail, *the present work does provide the first clear demonstration that the tetrahedral stereoisomer is not exclusively populated in Co(II) complexes, which by virtue of their structural features, are not constrained to be either tetrahedral or planar.*[45]

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[45] The bis(salicylaldimino) complexes **1** with R = H and OH may be planar to an unknown extent in solution.[36] However, the spectra purported to demonstrate this structure are apparently mislabeled and do not convincingly resemble the spectrum of the planar model, N,N-bis-(salicylidene)ethylenediaminocobalt(II) (*cf.* Figure 3 in ref 36).

Rotational Conformers of Glutaronitrile in Complexes with Metal Ions

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Contribution from the Department of Chemistry, Harvey Mudd College, Claremont, California. *Received January 21, 1966*

Abstract: Infrared spectra have been utilized to characterize rotational conformations of glutaronitrile[2] in the compounds $Cu(gn)_2ClO_4$, $Ag(gn)_2ClO_4$, $Ag(gn)_2BF_4$, $3.75AgNO_3 \cdot (gn)$, $TiCl_4 \cdot (gn)$, and $SnCl_4 \cdot (gn)$. Glutaronitrile assumes the GG rotational conformation[3] in the complexes with silver(I) and copper(I) and the TT conformation in the complexes with tin(IV) and titanium(IV).

Among the four spectroscopically distinguishable rotational conformers, TT, GG, GG′, and TG of glutaronitrile,[3] the assignment of infrared frequencies of the TT conformer has eluded cogent verification. The TT conformer is absent in the solid state at low temperatures,[4] and its concentration in the liquid state is unknown. The population of the GG′ conformer can be assumed to be negligible because of steric reasons. The more stable of two solid modifications of gn has been identified as the GG conformer,[4] the conformation of the ligand in $Cu(gn)_2NO_3$.[5] The absence of certain key frequencies in the spectrum of the metastable modification of gn led to its assignment as the TG conformation.[4,6] While the existence of the metastable modification of gn was questioned in a recent adiabatic calorimetric study,[7] a differential scanning calorimetric study demonstrated the existence of the metastable modification and provided evidence in support of the assignment of the TG conformation to the metastable modification.[8] However, since the relative amounts of the metastable modification present depend on the rate of cooling of liquid gn, the rotational conformational purity of the metastable modification is still unknown. That mixtures of rotational conformers can exist in solid dinitriles is exemplified by mixtures of *trans* and *gauche* conformers in solid succinonitrile from 230 to 329°K.[9,10]

After subtracting absorption due to the solid TG and GG modifications from the spectrum of liquid gn, the remaining bands (all of very low intensities with the exception of a strong band at 737 cm^{-1}) were assigned to the TT conformer.[4,6] If the intense band at 737 cm^{-1} is indicative of a high concentration of the TT conformer in liquid gn,[11] it is noteworthy that almost all of the other frequencies presently assigned to the TT conformer are of exceedingly low intensity. Frequencies of the TT conformer coincident with those of the TG and GG conformers could not be detected by the subtractive method of Matsubara.[4,6]

It was of interest in this study to investigate whether the TT conformer of gn would be assumed in complexes with metal ions and to determine whether these results may be used in making spectral assignments for gn. Infrared spectral studies of complexes have been extremely valuable in establishing assignments of frequencies to the *trans* and *gauche* conformers of succinonitrile.[10,12,13]

Experimental Section

Materials. Eastman White Label glutaronitrile was refluxed over phosphorus pentoxide and fractionated *in vacuo*. Anhydrous

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[1] Petroleum Research Fund Undergraduate Research Scholar, 1965.

[2] The symbol gn is used for glutaronitrile.

[3] For nomenclature of rotational conformers, see S. Mizushima, "Structures of Molecules and Internal Rotation," Part I, Academic Press Inc., New York, N. Y., 1954, Chapter V.

[4] I. Matsubara, *J. Chem. Phys.*, **35**, 373 (1961).

[5] Y. Kinoshita, I. Matsubara, and Y. Saito, *Bull. Chem. Soc. Japan*, **32**, 1216 (1959).

[6] I. Matsubara, *ibid.*, **34**, 1719 (1961).

[7] H. L. Clever, C. A. Wulff, and E. F. Westrum, Jr., *J. Phys. Chem.*, **69**, 1983 (1965).

[8] M. Kubota and G. O. Spessard, *ibid.*, 70, 941 (1966).

[9] (a) W. E. Fitzgerald and G. J. Janz, *J. Mol. Spectry.*, **1**, 49 (1957); (b) T. Fujiyama, K. Tokumaru, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 415 (1964).

[10] I. Matsubara, *J. Chem. Soc. Japan*, **34**, 1710 (1964).

[11] The mole fraction of the TT conformer of gn vapor at 298°K has been estimated to be 0.43. See ref 7.

[12] M. Kubota and S. R. Schulze, *Inorg. Chem.*, **3**, 853 (1964).

[13] M. Kubota, D. L. Johnston, and I. Matsubara, *ibid.*, **5**, 386 (1966).