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The Solution Stereochemistry of Four-Coordinate Bis(chelate)metal(II) Complexes. Further Experimental Results and a Summary of Stereochemical Trends

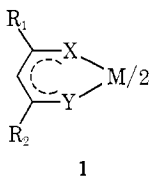
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In order to expand the existing body of stereochemical information on bis(chelate)metal(II) complexes, four series of bis- β -ketoamino complexes of the type $M[C_6H_5COCHCN(R)CH_3]_2$ have been synthesized: $M = Cr(II)$ ($R = CH_3, i-C_3H_7$), $Fe(II)$ ($R = H, CH_3, i-C_3H_7$), $Cu(II)$ ($R = H, CH_3, i-C_3H_7$), and $Zn(II)$ ($R = H, CH_3$). The $Cr(II)$ and $Fe(II)$ series are of particular interest for they include some of the few well-characterized four-coordinate chelates of these metal ions. Ligand field spectral, magnetic, and X-ray data indicate that the $Cr(II)$ and $Fe(II)$ complexes are planar and tetrahedral, respectively, and that two $Cu(II)$ complexes ($R = H, CH_3$) are planar. $Cu[C_6H_5COCHCN(i-C_3H_7)CH_3]_2$ apparently possesses a somewhat distorted, presumably pseudotetrahedral structure. This structural information has been combined with that previously obtained for the analogous $Co(II)$ and $Ni(II)$ bis(β -ketoamines) and for other bis chelates of general type 1, and a number of conclusions have been drawn relative to the stereochemical patterns exhibited by a wide group of bis chelates containing donor sets of differing steric and electronic properties.

Introduction

In our previous studies of the factors which control the stereochemistry of four-coordinate metal(II) chelate complexes,²⁻⁷ species of general formulation 1 have been employed. As has been pointed out earlier,⁵ the



particular advantage of complexes of this type is that the substituents R_1 and R_2 and, more significantly, the donor sets X_2Y_2 can be varied without undue synthetic difficulty so as to reveal the differential stereochemistry of members of two series: (i) complexes with constant ligand structure and varying metal ion and (ii) complexes of varying ligand structure and the same metal ion. A further advantage of type 1 complexes is that, with suitable R_1 and R_2 substituents, they are resistant to oligomerization and sufficiently soluble in nonpolar or weakly polar organic solvents to permit measurement of spectral and magnetic properties required for determination of stereochemistry, which should not be strongly influenced by the solvent medium.

In determining the stereochemical patterns of the complexes 1 in series (i) and (ii), two groups of donor sets may be distinguished. The sets $X_2Y_2 = O_4, S_4, O_2S_2, O_2(NH)_2, S_2(NH)_2$, and, possibly, $(NH)_4$ present little if any purely steric effects on the relative stabilities of the limiting planar and tetrahedral stereoisomers. Hence, the structures—particularly the solution structures—of complexes containing these sets in series (i) and (ii) are those which are rendered the more stable

by the concerted electronic effects of metal ion and donor atoms. The most extensive series (i) is that of the $M-O_4$ type, composed of the bis-dipivaloylmethanido complexes $M(dpm)_2$ (1, $R_1 = R_2 = t-C_4H_9$) of $Cr(II)-Zn(II)$.⁷ In this series all complexes are tetrahedral except $Cr(dpm)_2$, $Ni(dpm)_2$, and $Cu(dpm)_2$. While this structural pattern is found in the only other equally extensive series of bis chelates, the bis[dihydrobis(1-pyrazolyl)borates],⁸ its generality with respect to other nonsterically active X_2Y_2 sets cannot be fully assessed at present. Although $M-X_2Y_2$ complexes with these donor sets and $M = Ni(II), Cu(II),$ and $Zn(II)$ are known⁹⁻¹² or may be confidently assumed to adhere to this pattern, few monomeric chelates of divalent metal ions lying to the left of cobalt in the first transition series have been prepared. The available results for a number of $Co(II)$ systems reveal that a structural transition occurs with complexes comprising series (ii). Of the three $Co-O_2S_2$ complexes whose structures have been established in solution, two are tetrahedral and the other, bis(monothiodipivaloylmethanido)cobalt(II), is involved in a planar \rightleftharpoons tetrahedral equilibrium.⁷ All six of the known $Co-O_2(NH)_2$ complexes show this structural equilibrium in solution,^{3,4} with the proportion of stereoisomers dependent upon R_1 and R_2 . The most thoroughly characterized

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(1) Petroleum Research Fund Predoctoral Fellow, 1968-1969.

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(4) G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

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

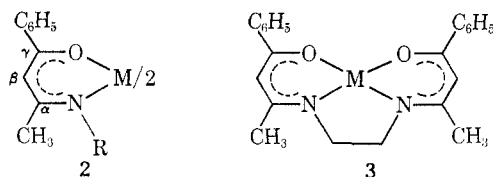
Complex	Mp, °C	Calcd %			Found %		
		C	H	N	C	H	N
Cr(<i>i</i> -C ₃ H ₇ -C ₆ H ₅ HCH ₃) ₂	148-150	68.39	7.07	6.14	68.28	7.16	5.84
Cr(CH ₃ -C ₆ H ₅ HCH ₃) ₂	194-195	65.98	6.04	7.00	65.81	6.21	7.06
Cr(-CH ₂ -C ₆ H ₅ HCH ₃) ₂	309-310	66.32	5.57	7.03	65.69	5.71	7.00
Fe(<i>i</i> -C ₃ H ₇ -C ₆ H ₅ HCH ₃) ₂	181-183	67.83	7.02	6.07	67.74	7.15	6.20
Fe(CH ₃ -C ₆ H ₅ HCH ₃) ₂	225-226	65.35	6.00	6.93	64.62	5.92	6.78
Fe(H-C ₆ H ₅ HCH ₃) ₂	168-170	63.85	5.36	7.45	63.65	5.32	7.26
Fe(Cyh-C ₆ H ₅ HCH ₃) ₂ ^a	178-180	71.09	7.47	5.18	70.81	7.44	5.39
Fe(<i>i</i> -C ₃ H ₇ - β -NaphHCH ₃) ₂ ^b	231-233	72.86	6.47	5.00	72.42	6.52	5.05
Cu(<i>i</i> -C ₃ H ₇ -C ₆ H ₅ HCH ₃) ₂	168-169	66.72	6.89	5.98	66.98	7.20	6.27
Cu(CH ₃ -C ₆ H ₅ HCH ₃) ₂	188-190	64.14	5.87	6.80	63.95	5.63	6.79
Cu(H-C ₆ H ₅ HCH ₃) ₂	201-203	62.57	5.25	7.29	62.75	5.27	7.31
Cu(<i>i</i> -C ₃ H ₇ -CH ₃ HCH ₃) ₂	106-108	55.87	8.21	8.14	55.90	8.16	8.23
Zn(CH ₃ -C ₆ H ₅ HCH ₃) ₂	198-200	63.86	5.85	6.77	64.01	6.01	6.68
Zn(H-C ₆ H ₅ HCH ₃) ₂	172-174	62.27	5.22	7.26	62.11	5.23	7.07

^a Cyh = cyclohexyl. ^b β -Naph = β -naphthyl.

Co-S₄ complex, bis(dithioacetylacetonato)cobalt(II),^{9a} is planar,¹³ as is the only reported Co-(NH)₄ species, bis(pent-2-en-4-imino-2-aminato)cobalt(II).¹²

The second group of donor sets consists of O₂(NR)₂ and S₂(NR)₂, in which the R group (alkyl or aryl) may be readily varied over a range of steric effects. In this way differing degrees of steric strain can be incorporated in the *trans*-planar form, producing in many but not all cases (*vide infra*) a partial or complete destabilization of this isomer relative to the tetrahedral form.^{2-4,6} The use of these donor sets in type 1 complexes has permitted a detailed study of the relative stereochemical and electronic effects of oxygen and sulfur donor atoms in Ni-O₂(NR)₂ and Ni-S₂(NR)₂ complexes⁶ and determination of the relative stereochemical populations of a number of [Co-O₂(NR)₂]-[Ni-O₂(NR)₂] pairs of complexes (R = H, CH₃).^{3,4}

The purpose of the present study is twofold. First, a further experimental definition of stereochemical patterns in series (i) and (ii) has been attempted by the preparation and physical studies of the bis(β -ketoamino)chromium(II), -iron(II), and -copper(II) complexes with R = H, CH₃, and *i*-C₃H₇. In this connection several tetradentate complexes **3** have been prepared for use as approximate models for the planar forms of **2**. Second, the structural information obtained has been integrated with that from earlier



work by ourselves^{2-4,6,7} and others on type 1 complexes of Cr(II)-Zn(II) with the same or different donor sets in order to present a comprehensive picture of the stereochemical trends in the two series.

As in previous reports^{2-4,6} bis- β -ketoamino complexes are designated as M(R-R _{β} R _{α})₂ in which the R's refer to the chelate ring substituents. Type 2 and 3

complexes are thus abbreviated as M(R-C₆H₅HCH₃)₂ and M(-CH₂-C₆H₅HCH₃)₂, respectively.

Experimental Section

Preparation of Compounds. (a) **Ligands.**—The ligands employed in this investigation were synthesized by condensing the appropriate β -diketones with primary amines in absolute ethanol solutions under reflux. The resulting α,β -unsaturated β -ketoamines were purified by distillation or recrystallization and were characterized by their melting points and/or pmr spectra. All ligands have been prepared previously.²⁻⁴

(b) **Complexes.**—All of the complexes utilized in this investigation are reactive to various degrees with oxygen and/or water. In order to isolate pure products it was necessary to carry out all preparations, extractions, and recrystallizations with due precautions against oxidation and hydrolysis by the atmosphere. This was accomplished using glassware fitted with standard taper joints and side arms equipped with vacuum stopcocks.¹⁴ Chromium(II) and iron(II) complexes were exposed only to oil pump vacuum and rigorously purified nitrogen and were recrystallized from thoroughly degassed solvents. The oxidative stability of the compounds, in general, decreases in the order Co(II) > Fe(II) > Cr(II). For a given metal those complexes bearing large nitrogen substituents are more stable toward oxidation and hydrolysis than those with smaller groups. Solutions are more unstable than solids. Yields of purified complexes ranged from 50 to 80%. Characterization data for the complexes are presented in Table I.

Bis(β -ketoamino)chromium(II) Complexes.—The procedure used is the same modified nonaqueous chelation reaction employed for the preparation of bis(dipivaloylmethanido)chromium(II).⁷ Typically, a degassed solution of ~100 ml of freshly distilled tetrahydrofuran and 0.05 mol of ligand was cooled to -20° and treated dropwise with 32 ml of 1.6 N *n*-butyllithium (0.051 mol) in *n*-hexane. After 5 g (excess over required 0.0125 mol) of anhydrous chromous acetate was added, the mixture was warmed to room temperature and stirred for 4-6 hr. Following removal of the solvent *in vacuo* the solid residue was extracted with *n*-heptane or toluene or a mixture of the two solvents. Upon cooling to -20° for several hours the filtrate obtained from the extraction yielded brown or red crystals which were collected on a fritted filter. One additional recrystallization from the same solvent or solvent mixture yielded a pure product. The solvent used for Cr(*i*-C₃H₇-C₆H₅HCH₃)₂ was *n*-heptane, for Cr(CH₃-C₆H₅HCH₃)₂, a mixture of 80:20 toluene-*n*-heptane, and for Cr(-CH₂-C₆H₅HCH₃)₂, toluene. All of these compounds smoke and turn into a soft tar upon exposure to air and thus must be stored under an atmosphere of pure nitrogen. Chlorinated hydrocarbon solvents react with these compounds to form species

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(14) R. H. Holm, F. Röhrscheid, and G. W. Everett, Jr., *Inorg. Syn.*, **11**, 72 (1968).

which contain chromium(III). The magnetic moments of anaerobically prepared chloroform solutions of $\text{Cr}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$ and $\text{Cr}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$ are 3.5 and 3.9 BM, respectively. No attempts were made to characterize the reaction products.

When a *small* amount of solid $\text{Cr}(-\text{CH}_2\text{-C}_6\text{H}_5\text{HCH}_3)_2$ is exposed to air a crystalline state seems to be retained. The compound, which is originally dark red-brown, immediately turns black and after 2 days appears light red-brown. After such treatment the material possesses an analysis consistent with the formulation $\text{Cr}(-\text{CH}_2\text{-C}_6\text{H}_5\text{HCH}_3)_2 \cdot \frac{3}{2}\text{O}_2$. *Anal.* Calcd for $\text{C}_{22}\text{-H}_{22}\text{N}_2\text{O}_5\text{Cr}$: C, 59.18; H, 4.97; N, 6.28. Found: C, 59.34; H, 5.05; N, 6.12. No other characterization was performed on this compound.

Bis(β -ketoamino)iron(II) Complexes.—These complexes were prepared using the nonaqueous chelation procedure described for the preparation of the nickel(II) β -ketoamine² and β -thioamine⁶ complexes. The metal ion source was bis(tetraethylammonium) dichlorodibromoferrate(II) and the complexes were extracted and recrystallized from *n*-heptane or toluene. Pure products were isolated as red or brick red crystalline solids.

Bis(β -ketoamino)copper(II) Complexes.—All of these complexes except for $\text{Cu}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$ were prepared by the nonaqueous chelation procedure using *t*-butyl alcohol as the solvent.¹⁴ This compound was obtained by the method used for the synthesis of the chromium(II) complexes. Purification was achieved by recrystallization from *n*-heptane or toluene. $\text{Cu}(-\text{CH}_2\text{-C}_6\text{H}_5\text{HCH}_3)_2$ ¹⁵ and $\text{Cu}(\text{H-C}_6\text{H}_5\text{HCH}_3)_2$ ¹⁶ have previously been prepared by different methods.

Bis(β -ketoamino)zinc(II) Complexes.—These compounds were prepared and purified by the method described elsewhere.⁶

Bis(1-phenyl-3-*N*-isopropylamino-2-buten-1-ono)palladium(II).—This compound was prepared by the nonaqueous chelation procedure using *n*-butyllithium and tetrahydrofuran as the solvent and was isolated as an orange crystalline solid after recrystallization from toluene; mp 219–220°. *Anal.* Calcd for $\text{C}_{28}\text{H}_{32}\text{-O}_2\text{N}_2\text{Pd}$: C, 61.16; H, 6.32; N, 5.49. Found: C, 60.67; H, 6.20; N, 5.25.

Physical Measurements.—Because of the sensitivity of most of the complexes to traces of water and/or oxygen, all measurements were carried out in rigorously dry solvents, degassed when necessary, and whenever possible under a pure nitrogen atmosphere or *in vacuo*. Magnetic moments of complexes in the solid and solution phases were determined by the Gouy method using an aqueous nickel chloride solution and freshly boiled, distilled water as the calibrants, respectively. Electronic spectra were recorded on a Cary Model 14 spectrophotometer.

Molecular Weight Determination.—The molecular weight of $\text{Cr}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$ in benzene solution at 55° was determined isopiastically using benzil as the calibrant. The concentration of the complex and standard at equilibrium was 0.103 *M*. Molecular weight: calcd, 457; found, 458.

X-Ray Powder Data.—Powder photographs were obtained using a Philips Debye-Scherrer camera with a diameter of 114.6 mm. $\text{Cu K}\alpha$ radiation with an Ni filter was used. The samples were sealed in 0.2-, 0.3-, or 0.5-mm diameter lead-free borosilicate capillaries. The following interplanar spacings (Å) and visually estimated intensities were obtained: $\text{Cr}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$: 12.14 (vs), 7.21 (m), 6.03 (vs), 5.70 (m), 5.48 (s), 5.27 (w), 4.82 (vw), 3.91 (w), 3.84 (w), 3.73 (vw), 3.61 (vs), 3.42 (m), 3.31 (m), 3.18 (vw), 3.05 (vw), 2.96 (vw); $\text{Pd}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$: 12.23 (vs), 7.16 (m), 6.01 (vs), 5.87 (w), 5.65 (m), 5.46 (m), 5.26 (m), 4.79 (w), 3.91 (w), 3.83 (w), 3.69 (vw), 3.61 (s), 3.42 (m), 3.31 (m), 3.19 (w), 3.09 (w), 2.98 (vw); $\text{Cu}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$: 10.78 (vw), 9.39 (w), 8.60 (vs), 7.96 (m), 6.71 (vw), 6.54 (s), 5.93 (vw), 5.74 (s), 5.41 (m), 5.17 (m), 4.88 (w), 4.68 (m), 4.16 (vw), 3.97 (vw), 3.52 (s), 3.42 (w), 3.35 (vw), 2.37 (m); $\text{Cr}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$: 10.56 (s), 7.76 (vs),

TABLE II
MAGNETIC MOMENTS OF BIS(β -KETOAMINO)CHROMIUM(II),
-IRON(II), AND -COPPER(II) COMPLEXES

Complex	Solid μ_{eff} , BM	Solvent	Solution		
			Temp, °C	Concn, <i>m</i>	μ_{eff} , BM
$\text{Cr}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$	4.92	Toluene	24	59	4.85
$\text{Cr}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$	4.74	Toluene	19	25	4.62
$\text{Cr}(-\text{CH}_2\text{-C}_6\text{H}_5\text{HCH}_3)_2$	2.22	<i>a</i>			
$\text{Fe}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$	5.01	Chloroform	24	45	5.17
$\text{Fe}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$	5.06	Dichloromethane	23	62	5.08
$\text{Fe}(\text{H-C}_6\text{H}_5\text{HCH}_3)_2$	5.15	Chloroform	19	31	5.16
$\text{Fe}(i\text{-C}_3\text{H}_7\text{-}\beta\text{-NaphHCH}_3)_2$	5.15	Chloroform	23	55	5.13
$\text{Cu}(i\text{-C}_3\text{H}_7\text{-C}_6\text{H}_5\text{HCH}_3)_2$	1.98	Chloroform	21	55	1.86
$\text{Cu}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$	1.85	Chloroform	23	56	1.82
$\text{Cu}(\text{H-C}_6\text{H}_5\text{HCH}_3)_2$	1.83	Chloroform	23	69	1.77

^a Insufficiently soluble for measurement.

5.37 (s), 4.97 (s), 4.41 (vw), 3.90 (s), 3.52 (s), 3.30 (w), 3.16 (w), 2.65 (m), 2.26 (vw), 2.21 (vw), 2.02 (vw); $\text{Cu}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$: 10.16 (vs), 7.60 (s), 6.46 (s), 6.10 (w), 5.78 (m), 5.19 (s), 4.86 (w), 4.71 (w), 4.30 (m), 4.01 (w), 3.89 (vw), 3.77 (w), 3.63 (m), 3.49 (w), 3.38 (w), 2.88 (vw), 2.80 (vw), 2.53 (vw), 2.35 (w), 2.25 (vw), 2.11 (vw), 2.04 (vw); $\text{Ni}(\text{CH}_3\text{-C}_6\text{H}_5\text{HCH}_3)_2$: 13.09 (s), 6.80 (w), 5.78 (vs), 5.42 (w), 4.96 (w), 4.47 (vs), 3.73 (vs), 3.58 (s), 3.24 (m), 3.09 (s), 2.99 (m), 2.88 (w), 2.81 (m), 2.69 (w), 2.64 (m), 2.47 (w), 2.40 (s), 2.33 (w), 2.27 (w). The isomorphous relationships which can be deduced from the above data are discussed in the following sections.

Results and Discussion

The bis- β -ketoamino complexes 2 prepared and characterized in this work are listed in Table I. Their preparation and structural identification were undertaken in order to provide a series (i) $\text{M-O}_2(\text{NH})_2$ group of complexes comparable to the $[\text{M-O}_4](\text{M}(\text{dpm})_2)$ group. Previously, the preparation of the analogous Co(II) and Ni(II) complexes was reported and their structures in the solid state and in solutions of noncoordinating solvents were determined.²⁻⁴ In these earlier studies and in the present investigation three subgroups of complexes, defined by the nitrogen substituent R, were examined. These include the R = H, CH_3 , and $i\text{-C}_3\text{H}_7$ species in which the potential steric destabilization of the planar isomer ranges from essentially zero (H) to quite strong ($i\text{-C}_3\text{H}_7$). This order of destabilization has been observed in $\text{Ni}(\text{R-C}_6\text{H}_5\text{HCH}_3)_2$ complexes in chloroform solution for which the mole fractions of tetrahedral form (N_t) are the following at 25°:^{2,4} H, 0; CH_3 , 0.018; $i\text{-C}_3\text{H}_7$, 1. For the same series of Co(II) complexes under similar conditions these values have been obtained:^{3,4} H, 0.56; CH_3 , 1; $i\text{-C}_3\text{H}_7$, 1. Hence, changes in R can appreciably alter stereochemical distributions and offer a way of differentially populating the less stable isomer to a detectable extent in a group of β -ketoamino complexes which might be planar in the absence of steric destabilization. For this reason the indicated changes in the R group were made in the Cr(II), Fe(II), and Cu(II) series of complexes, with the single exception of $\text{Cr}(\text{H-C}_6\text{H}_5\text{HCH}_3)_2$, which could not be isolated in the pure condition. The Cr(II) and Fe(II) complexes in Table I constitute the majority of the very few discrete four-coordinate complexes of these metal ions which have been isolated.

Magnetic moments in the solid and solution phases

(15) P. J. McCarthy, R. J. Hovey, K. Ueno, and A. E. Martell, *J. Am. Chem. Soc.*, **77**, 5820 (1955).

(16) H. F. Holtzclaw, Jr., J. P. Collman, and R. M. Alire, *ibid.*, **80**, 1100 (1958).

TABLE III
 LIGAND FIELD SPECTRAL DATA FOR CHROMIUM(II), IRON(II), AND COPPER(II) BIS(β -KETOAMINO) COMPLEXES

Complex	Solvent	λ_{\max} , cm ⁻¹	ϵ , l. mol ⁻¹ cm ⁻¹ ^a
Cr(<i>i</i> -C ₃ H ₇ -C ₆ H ₅ HCH ₃) ₂	Toluene	~19,500 sh	~260
Cr(CH ₃ -C ₆ H ₅ HCH ₃) ₂	Benzene	18,700	200
Cr(-CH ₂ -C ₆ H ₅ HCH ₃) ₂	Toluene	18,500	~300 ^b
Fe(<i>i</i> -C ₃ H ₇ -C ₆ H ₅ HCH ₃) ₂	Chloroform	~9,000 sh, 11,200	25, 45
Fe(CH ₃ -C ₆ H ₅ HCH ₃) ₂	Dichloromethane	~9,500 sh, 12,500	~20, 47
Fe(H-C ₆ H ₅ HCH ₃) ₂	Dichloromethane	~9,500 sh, 11,800	~25, 46
Fe(<i>i</i> -C ₃ H ₇ - β -NaphHMe) ₂	Chloroform	11,200	55
Fe(Cyh-C ₆ H ₅ HCH ₃) ₂	Chloroform	~9,000 sh, 11,100	~30, 45
Cu(<i>i</i> -C ₃ H ₇ -C ₆ H ₅ HCH ₃) ₂	Chloroform	~13,800 sh	~110
Cu(CH ₃ -C ₆ H ₅ HCH ₃) ₂	Chloroform	16,000	96
Cu(H-C ₆ H ₅ HCH ₃) ₂	Chloroform	17,500	74
Cu(-CH ₂ -C ₆ H ₅ HCH ₃) ₂	Chloroform	~16,400 sh, 18,500	~132, 265

^a Uncorrected for underlying absorption. ^b Inaccurate due to low solubility.

and ligand field spectral data for the complexes in Table I are set out in Tables II and III.

Chromium(II) Complexes.—The electronic properties of these complexes and of Cr(dpm)₂, whose planar structure in the solid and in solution has been established recently,⁷ are quite similar. Like the latter compound, Cr(CH₃-C₆H₅HCH₃)₂ and Cr(*i*-C₃H₇-C₆H₅-HCH₃)₂ have quintet ground states in the solid and in solution. Their ligand field spectra in toluene solution are closely related, with the features at 18,700 and ~19,500 cm⁻¹ being the analogs of the similarly intense 23,000-cm⁻¹ band of Cr(dpm)₂ in toluene. The spectra are essentially unchanged in the solid state. They bear no relation to those of pseudotetrahedral CrX₄²⁻ species and CrX₂((C₆H₅)₃PO)₂,¹⁸ which show a single feature near *ca.* 10,000 cm⁻¹ assigned as the ⁵T₂ → ⁵E transition in idealized tetrahedral symmetry.

Further structural confirmation was sought from X-ray powder data. The patterns of Cr(CH₃-C₆H₅-HCH₃)₂ and Cu(CH₃-C₆H₅HCH₃)₂ display certain similarities but do not prove an isomorphous relationship. Neither of these powder patterns bears any significant resemblance to that of diamagnetic, planar Ni(CH₃-C₆H₅HCH₃)₂. However, a definite isomorphous relationship exists between Cr(*i*-C₃H₇-C₆H₅-HCH₃)₂ and Pd(*i*-C₃H₇-C₆H₅HCH₃)₂ but does not include Cu(*i*-C₃H₇-C₆H₅HCH₃)₂, the structure of which is considered in a following section. This result,¹⁹ together with the near coincidence of the spectral and

magnetic properties of Cr(CH₃-C₆H₅HCH₃)₂, Cr(*i*-C₃H₇-C₆H₅HCH₃)₂, and Cr(dpm)₂ in the solid and solution phases and the demonstrated monomerism of the isopropyl complex, strongly suggests planar structures for the β -ketoamine complexes.

Additional investigation of the electronic properties of planar chromium(II) β -ketoamines was attempted by the preparation of Cr(-CH₂-C₆H₅HCH₃)₂ (3). This complex was isolated as an air-sensitive red-brown solid whose low solubility in noncoordinating solvents is suggestive of an associated structure. The magnetic moment of 2.22 BM is not consistent with monomeric Cr(II) and might arise by spin interaction *via* oxygen bridges in a dimeric structure such as that of N,N'-bis(salicylidene)ethylenediamino copper(II).²¹

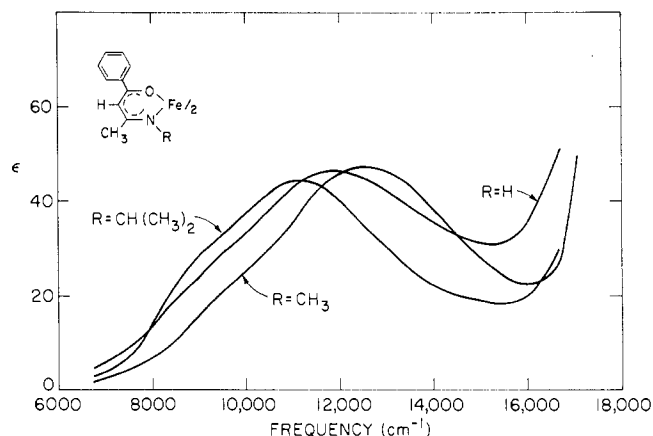


Figure 1.—Ligand field spectra of Fe(H-C₆H₅HCH₃)₂ and Fe(CH₃-C₆H₅HCH₃)₂ in dichloromethane and of Fe(*i*-C₃H₇-C₆H₅HCH₃)₂ in chloroform.

(17) D. M. Gruen and R. L. McBeth, *Pure Appl. Chem.*, **6**, 23 (1963); D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, **5**, 479 (1966).

(18) D. E. Scaife, *Australian J. Chem.*, **20**, 845 (1967).

(19) Although the isomorphism between the Cr(II) and Pd(II) complexes provides some evidence for the gross planar structure of the former, any type of distortion from overall molecular planarity necessitated by the bulkiness of the isopropyl groups remains uncertain. A considerable body of X-ray evidence makes clear two well-defined types of distortions that alleviate steric crowding in bis chelates which otherwise might be expected to approach overall planarity. One of these is a torsional distortion toward a tetrahedral structure and has been observed for Ni(II)^{3,4} and Cu(II) complexes (*vide infra*). The second is the adoption of a stepped structure in which the coordination sphere is planar but the mean planes of the ligands are not coplanar. Sterically encumbered Pd(II) chelates have not been observed to undergo torsional distortion. A potentially relevant case here is bis(*N*-*t*-butylsalicylaldiminato)palladium(II),²⁰ which possesses a *trans*-planar Pd-O₂N₂ coordination unit and a step distance of 1.7 Å between the salicylaldimine residues. In view of the isomorphism of Cr(*i*-C₃H₇-C₆H₅-HCH₃)₂ with Pd(*i*-C₃H₇-C₆H₅HCH₃)₂, but not with the Cu(II) analog, it is possible that the first two complexes possess stepped structures, at least in the crystalline state.

(20) V. W. Day, M. D. Glick, and J. L. Hoard, *J. Am. Chem. Soc.*, **90**, 4803 (1968).

(21) D. Hall and T. N. Waters, *J. Chem. Soc.*, 2644 (1960).

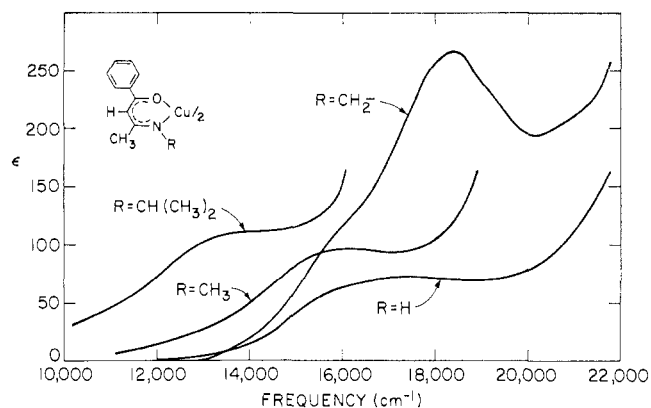
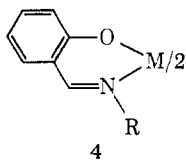


Figure 2.—Ligand field spectra of $\text{Cu}(\text{H}-\text{C}_6\text{H}_5\text{HCH}_3)_2$, $\text{Cu}(\text{CH}_3-\text{C}_6\text{H}_5\text{HCH}_3)_2$, $\text{Cu}(i\text{-C}_3\text{H}_7-\text{C}_6\text{H}_5\text{HCH}_3)_2$, and $\text{Cu}(-\text{CH}_2-\text{C}_6\text{H}_5\text{HCH}_3)_2$ in chloroform.

cm^{-1} . In all cases these absorptions are assigned as components of the ${}^5\text{E} \rightarrow {}^5\text{T}_2$ transition in T_d symmetry which is split by the actual symmetry (D_{2d} or lower) of the complexes. Two other complexes, $\text{Fe}(\text{C}_6\text{H}_5\text{-HCH}_3)_2$ and $\text{Fe}(i\text{-C}_3\text{H}_7\text{-}\beta\text{-NaphHCH}_3)_2$, were also prepared and found to have electronic properties nearly indistinguishable from those of the other three β -ketoamine complexes. All five are assigned a tetrahedral structure in solution and in the solid.

Attempts to prepare $\text{Fe}(-\text{CH}_2-\text{C}_6\text{H}_5\text{HCH}_3)_2$ in order to compare the properties of the above bis chelates with those of a planar iron(II)- β -ketoamine complex failed. With the exception of a number of phthalocyanine and porphyrin complexes, examples of planar Fe(II) systems are rare. Indeed, in only one instance is structural documentation available for such a coordination unit. Planar coordination occurs in the mineral gillespite, which contains an axially unperturbed $\text{Fe}-\text{O}_4$ grouping.²² The spectrum of this high-spin chromophore is unrelated to that of any of the bis chelates examined in this work. Recently, N,N'-bis(salicylidene)ethylenediamineiron(II)²³ and a series of its ring-substituted derivatives^{23a} have been prepared and studied. The complexes are high-spin and magnetically dilute in the solid state, but unfortunately ligand field bands were not observed due to masking by charge-transfer absorptions.^{23a} High-spin bis(N-R-salicylaldiminato)iron(II) complexes (**4**, $\text{R} = \text{CH}_3, \text{C}_6\text{H}_5$) have also been reported.^{23a} On the basis of the results



obtained for the β -ketoamines, it is considered likely that these two complexes are also tetrahedral.

Cobalt(II) and Nickel(II) Complexes.—The prepara-

(22) R. G. Burns, M. G. Clark, and A. J. Stone, *Inorg. Chem.*, **5**, 1268 (1966).

(23) (a) A. Earnshaw, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.*, **A**, 1048 (1968); (b) F. Calderazzo, C. Floriani, R. Henzi, and F. L'Epplattenier, *ibid.*, **A**, 1378 (1969).

tion and stereochemistry of the $\text{M}(\text{R}-\text{C}_6\text{H}_5\text{HCH}_3)_2$ group of complexes with $\text{R} = \text{H}, \text{CH}_3$, and $i\text{-C}_3\text{H}_7$ and $\text{M} = \text{Co}(\text{II})^{3,4}$ and $\text{Ni}(\text{II})^{2-4}$ have previously been described and pertinent results are summarized above and in a following section.

Copper(II) Complexes.—The $\text{Cu}(\text{R}-\text{C}_6\text{H}_5\text{HCH}_3)_2$ series with $\text{R} = \text{H}, \text{CH}_3$, and $i\text{-C}_3\text{H}_7$ has been prepared. The *trans*-planar structure of crystalline $\text{Cu}(\text{H}-\text{C}_6\text{H}_5\text{-HCH}_3)_2$ has been established by a recent X-ray study.^{11b} The most significant feature of this group of complexes is that the solid and solution magnetic moments increase in the order $\text{H} < \text{CH}_3 < i\text{-C}_3\text{H}_7$ (*cf.* Table III) while the maxima of the lowest energy ligand field bands, which are undoubtedly composites of several transitions, shift in the opposite order (*cf.* Figure 2). This behavior bears a certain resemblance to that of a series of bis(N-R-salicylaldiminato)copper(II) complexes (**4**). Those with $\text{R} = \text{H}, \text{CH}_3, n\text{-C}_3\text{H}_7$, and $n\text{-C}_4\text{H}_9$ possess a planar $\text{Cu}-\text{O}_2\text{N}_2$ coordination unit in the solid state²⁴ whereas those with $\text{R} = \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$, and $t\text{-C}_4\text{H}_9$ are pseudotetrahedral²⁵ with dihedral angles of 36, 60, and 54°, respectively, between the CuON planes. Complexes of the first type exhibit similar solution and reflectance spectra,²⁶ $\mu_{\text{eff}} \leq 1.86$ BM in the solid and in solution,^{26a,27} and small dipole moments.^{26a,27,28} The crystalline pseudotetrahedral species also possess similar solid state and solution spectra,²⁶ which are characterized by a decided red shift of the lowest energy ligand field absorptions compared to the planar complexes. The solid and solution magnetic moments are apparently larger, with $\mu_{\text{eff}} \geq 1.89$ BM considered characteristic of nonplanar geometry,^{26a,27b,29} and dipole moments^{26a} are usually greater than those of the planar complexes. Two other groups of bis-(chelate)copper(II) complexes show approximately the same dependence of magnetic and spectral properties on the nature of the nitrogen substituent, *viz.*, the bis- β -iminoaminato¹² (**1**, $\text{X} = \text{Y} = \text{NR}$, $\text{R} = \text{H}, \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5$) and bis-pyrrole-2-aldeiminato³⁰ ($\text{R} = n\text{-C}_3\text{H}_7, i\text{-C}_3\text{H}_7, t\text{-C}_4\text{H}_9$) complexes. In particular, bis-(N-*t*-butylpyrrole-2-aldeiminato)copper(II) in two crystalline modifications has an average dihedral angle of

(24) $\text{R} = \text{H}$: E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.*, **A**, 680 (1966); $\text{R} = \text{CH}_3$: E. C. Lingafelter, G. L. Simmons, B. Morosin, C. Sheringer, and C. Freiberg, *Acta Cryst.*, **14**, 1222 (1961); $\text{R} = n\text{-C}_3\text{H}_7$: G. Bombieri, C. Panattoni, E. Farsellini, and R. Graziani, *ibid.*, **B25**, 1208 (1969); $\text{R} = n\text{-C}_4\text{H}_9$: D. Hall, R. H. Sumner, and T. N. Waters, *J. Chem. Soc.*, **A**, 420 (1969).

(25) $\text{R} = \text{C}_2\text{H}_5$: C. Panattoni, G. Bombieri, and R. Graziani, *Acta Cryst.*, **23**, 537 (1967); E. N. Baker, G. R. Clark, D. Hall, and T. N. Waters, *J. Chem. Soc.*, **A**, 251 (1967); $\text{R} = i\text{-C}_3\text{H}_7$: P. L. Orioli and L. Sacconi, *J. Am. Chem. Soc.*, **88**, 277 (1966); $\text{R} = t\text{-C}_4\text{H}_9$: T. P. Cheeseman, D. Hall, and T. N. Waters, *J. Chem. Soc.*, **A**, 685 (1966).

(26) (a) L. Sacconi and M. Ciampolini, *ibid.*, 276 (1964); (b) T. P. Cheeseman, D. Hall, and T. N. Waters, *ibid.*, **A**, 694 (1966).

(27) (a) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Inorg. Nucl. Chem.*, **19**, 73 (1961); (b) L. Sacconi, M. Ciampolini, and U. Campigli, *Inorg. Chem.*, **4**, 407 (1965).

(28) L. Sacconi, M. Ciampolini, F. Maggio, and G. Del Re, *J. Am. Chem. Soc.*, **82**, 815 (1960).

(29) Recent measurements of the solid $\text{R} = i\text{-C}_3\text{H}_7$ and $t\text{-C}_4\text{H}_9$ complexes (1.84, 1.83 BM, respectively) indicate that the magnetic moment ranges for the planar and pseudotetrahedral complexes may not be distinct: *cf.* B. N. Figgis, M. Gerloch, J. Lewis, and R. C. Slade, *J. Chem. Soc.*, **A**, 2028 (1968).

(30) R. H. Holm, A. Chakravorty, and I. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966).

60°³¹ and a larger magnetic moment and lower energy ligand field absorption than its *n*- and *i*-C₃H₇ analogs.

On the basis of the information just summarized, of which that for the copper(II) salicylaldimines is the most pertinent, it appears probable that in the Cu(R-C₆H₅HCH₃)₂ series distortion from a planar structure occurs as the size of R increases. A significantly nonplanar structure is considered likely only for Cu(*i*-C₃H₇-C₆H₅HCH₃)₂, principally because of its spectral dissimilarity to the CH₃ and H complexes and the pronounced tendency of α -branched alkyl groups to effect pseudotetrahedral distortions in copper(II) salicylaldimines^{25,26} and to stabilize the tetrahedral forms of nickel(II) salicylaldimine³² and β -ketoamine² complexes. A second possibility is the existence of a planar \rightleftharpoons tetrahedral equilibrium similar to that established for cobalt(II) and nickel(II) β -ketoamines.²⁻⁴ This equilibrium has actually been proposed for copper(II) salicylaldimines, β -ketoamines, and pyrrole-2-aldehydes on the basis of pmr³³ and dipole moment³⁴ data. However, these data do not allow a positive distinction between a rapid equilibrium and the presence of a single structural species of intermediate stereochemistry. Because crystalline pseudotetrahedral copper(II) salicylaldimines on the basis of electronic spectral data appear to retain essentially the same configuration in solution, it is concluded that Cu(*i*-C₃H₇-C₆H₅HCH₃)₂ is more likely to exist in a distorted, nonplanar form than to be involved in a structural equilibrium.

Zinc(II) Complexes.—Those with R = H and CH₃ were prepared; Zn(*i*-C₃H₇-C₆H₅HCH₃)₂ was reported earlier.⁶ These complexes are undoubtedly tetrahedral, as are the Zn(II) salicylaldimines in the crystalline^{35a,b} and solution^{35c} phases and all other four-coordinate Zn(II) complexes whose structures have been established. The pmr spectrum of Zn(*i*-C₃H₇-C₆H₅-HCH₃)₂ provides some further evidence for a tetrahedral configuration. Four signals in the form of two spin doublets ($J_{\text{HCH}_3} = 6$ cps) centered at -0.70 and -0.72 ppm are observed for the isopropyl methyl groups in deuteriochloroform solution at ambient temperature. These features are retained as the temperature increases, until above ca. 120° the two doublets collapse to one doublet. This behavior is consistent with a tetrahedral structure, which is dissymmetric and renders the methyl groups of each isopropyl substituent diastereotopic. The coalescence of the chemically shifted doublets at the higher temperatures is presumably due to racemization of the complex, which averages the chemical shifts of the methyl groups. In contrast, Pd(*i*-C₃H₇-C₆H₅HCH₃)₂ in deuteriochloro-

form shows one isopropyl methyl doublet at -0.95 ppm ($J_{\text{HCH}_3} = 7$ cps). Similar chemical shift separations of potentially diastereotopic groups have been observed in the pmr spectra of several other Zn(II) bis chelates and are currently being investigated as a means of measuring racemization rates.

Summary of Stereochemical Trends.—Sufficient structural information has now been accumulated in this and other investigations cited earlier that stereochemical patterns for partial or relatively complete series of complexes (i) and (ii), defined at the outset, may now be recognized. These patterns are summarized in Table IV. Horizontal and vertical rows

TABLE IV
STEREOCHEMICAL PATTERNS OF
BIS(CHELATE)METAL(II) COMPLEXES 1^a

Donor set X ₂ Y ₂	Cr- (II)	Mn- (II)	Fe- (II)	Co(II)	Ni(II)	Cu- (II)	Zn- (II)
O ₄	P ^b	T ^{b,c}	T ^b	T ^{b,d}	P ^d	P ^d	T ^d
(NH) ₄	e	e	e	P ^f	P ^f	P ^f	e
S ₄	e	e	e	P ^{b,g}	P ^h	e	e
O ₂ (NH) ₂	e	e	T	P \rightleftharpoons T ^{i-k}	P ^k	P ^l	T ^c
O ₂ S ₂	e	e	T ^b	T, ^b P \rightleftharpoons T ^{b,i,m}	P ⁿ	e	T ^c
O ₂ (NCH ₃) ₂	P	e	T	T ^o	P \rightleftharpoons T ^{i-k}	P	T ^c
O ₂ (N- <i>i</i> -CaH) ₂	P	e	T	T ^o	T ^q	pT	T ^p
(NCH ₃) ₄	e	e	e	T ^f	T ^f	pT ^f	e
S ₂ (NCH ₃) ₂	e	e	e	e	P \rightleftharpoons T ^{i,j,p}	e	T ^{c,p}

^a Information summarized refers to stereochemistry in non-coordinating solvents at or near room temperature. References to previously published structural determinations in solid and solution phases are entered as footnotes; any differences between solid and solution structures are noted. Symbols: P, planar; T, tetrahedral; pT, pseudotetrahedral. ^b Reference 7. ^c Complex of this type known; indicated structure assumed. ^d See literature cited in ref 7. ^e Complex of this type has not been prepared. ^f Reference 12. ^g Reference 13. ^h Reference 9. ⁱ Equilibrium position dependent upon substituents R₁ and R₂. ^j Solid complex(es) planar. ^k References 3 and 4. ^l Reference 11. ^m Single example known—bis(monothiodipivaloylmethanido)cobalt(II). ⁿ References 9b,c and 10. ^o Reference 3. ^p Reference 6. ^q References 2 and 4.

comprise series (i) and (ii), respectively. The information given refers to the stereochemistry of complexes of the general type 1 in noncoordinating solvents at or near room temperature. Structures of the crystalline complexes are in most cases the same as those indicated; any exceptions are entered as footnotes. The chelate ring substituents R₁ and R₂ are not specified inasmuch as they usually have a secondary effect on structure compared to changes in the donor sets. Their nature does affect the exact positions, but in nearly all cases^{36,37} not the occurrence, of the planar \rightleftharpoons tetrahedral structural equilibria noted.

Inspection of Table IV reveals that the largest amount of structural data is available for Ni(II) and Co(II), a smaller amount for Fe(II) and Cr(II), and

(31) C.-H. Wei, unpublished results; private communication, March 1967.

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

(33) H. P. Fritz, B. M. Golla, H. J. Keller, and K. E. Schwarzshans, *Z. Naturforsch.*, **21b**, 725 (1966).

(34) V. I. Minkin, O. A. Osipov, and D. Sh. Verkhovodova, *Russ. J. Inorg. Chem.*, **11**, 1522 (1966); V. P. Kurbatov, O. A. Osipov, and K. N. Kovalenko, *ibid.*, **13**, 228 (1968); O. A. Osipov, A. D. Garnovskii, and V. I. Minkin, *J. Struct. Chem.*, **8**, 817 (1967).

(35) (a) E. Prasson and C. Panattoni, *Z. Krist.*, **116**, 154 (1961); (b) L. Sacconi and P. L. Orioli, *Ric. Sci. Rend.*, **32**, 645 (1962); (c) L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **85**, 411 (1963).

(36) Two exceptions are to be noted. Of the three structurally characterized Co-Os₂ complexes, bis(monothioacetylacetonato)- and bis-(thiobenzoylacetonato)cobalt(II) are completely tetrahedral or nearly so in solution whereas bis(monothiodipivaloylmethanido)cobalt(II) is involved in the structural equilibrium.⁷ Bis(β -ketoamino)- and bis(β -thioamino)-nickel(II) complexes with hydrogen as the α substituent (*cf.* 2) populate the planar form to a greater extent than do the analogous α -methyl complexes with the same nitrogen substituents.^{2,6,37} The structural data in Table IV refer to species with R₁, R₂ \neq H.

(37) R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Am. Chem. Soc.*, **89**, 6104 (1967).

no definite structural information for Mn(II). Of the relevant Mn(II) species, only Mn(dpm)₂ has been prepared and its structure has not been proven.⁷ In terms of donor sets, data are incomplete for (NH)₄, S₄, (NCH₃)₄, and S₂(NCH₃)₂ in particular. Nonetheless, the available information does permit the following conclusions to be drawn, two of which are most simply expressed in relation to Ni(II) stereochemistry.

(a) Ligands which stabilize no measurable amount ($\lesssim 0.1\%$ ³⁸) of tetrahedral Ni(II) produce $\sim 100\%$ planar Cr(II) and planar (undistorted) Cu(II) and may stabilize $\sim 100\%$ planar or tetrahedral Co(II) or an equilibrium mixture of isomers dependent upon the donor atom set.

(b) The order of stabilization of planar Co(II) by X₂Y₂ donor sets is S₄ \sim (NH)₄ > O₂(NH)₂ \gtrsim O₂S₂ > O₄ \sim O₂(NR)₂.

(c) Ligands which stabilize a measurable amount ($\gtrsim 0.1\%$ ³⁸) of tetrahedral Ni(II) produce $\sim 100\%$ tetrahedral Co(II), tetrahedral Fe(II), and planar Cr(II).

(d) In Co(II) and Ni(II) complexes which are identical except for the donor sets, replacement of oxygen by sulfur increases the relative stability of the planar form, as indicated in (a) for Co(II) and by the order S₂(NR)₂ > O₂(NR)₂ for Ni(II).⁶

These conclusions, while applying specifically to type I complexes under similar experimental conditions, may in fact be reasonable generalizations. Thus, (a) and (c) apply to bis-chelate complexes of dihydrobis(1-pyrazolyl)borates,⁸ pyrrole-2-aldimines,³⁰ salicylaldimines,³² and aminotroponeimines.³⁹ Conclusions (b) and (d) cannot be more widely assessed at present because appropriate complexes other than **1** have not been prepared. It is to be noted that the converse of (c) is not necessarily true. This may be illustrated by several groups of complexes, among them the bis-(N-*n*-butylsalicylaldimines). The Ni(II) complex exists only in the planar form in dilute solution as indicated by its lack of contact shifts and is planar in the solid,⁴⁰ while the Co(II) complex is fully tetrahedral in the solid^{35a} and in solution.⁴¹ Additionally, it is relevant to point out that further investigation is required to determine if ligands of the type indicated in (a) will generate only one stereoisomer of Fe(II). The available information indicates that tetrahedral isomers are formed by three such ligands, but does

(38) A conservative estimate of the sensitivity of the contact shift method in detecting the tetrahedral isomer.

(39) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963); W. R. McClellan and R. E. Benson, *ibid.*, **88**, 5165 (1966); D. R. Eaton, W. R. McClellan, and J. F. Weiher, *Inorg. Chem.*, **7**, 2040 (1968).

(40) E. Frasson, C. Panattoni, and L. Sacconi, *Gazz. Chim. Ital.*, **92**, 1470 (1962).

(41) L. Sacconi, M. Ciampolini, F. Maggio, and F. P. Cavasino, *J. Am. Chem. Soc.*, **84**, 3246 (1962).

not allow the prediction that Fe-S₄ and Fe-(NH)₄ complexes will possess this same structure, a point underscored by formation of only the planar isomers of the analogous Co(II) complexes. Attempts to reproduce the reported syntheses⁴² of bis(dithioacetylacetonato)iron(II) have thus far failed.

Planar Cr(II) has been included in (c) despite structural information on only three complexes. This has been done because the O₂(N-*i*-C₃H₇)₂ donor set produces only tetrahedral or pseudotetrahedral structures with five other metal ions but forms a Cr(II) complex which is isomorphous with its Pd(II) analog and possesses similar spectral properties to Cr(dpm)₂ and Cr(CH₃-C₆H₅HCH₃)₂, neither of which is subject to strong steric destabilization of the planar form. Thus, the (NH)₄, S₄, O₂(NH)₂, O₂S₂, and S₂(NCH₃)₂ complexes of Cr(II) are predicted to be planar.

The enthalpy and entropy quantities comprising free energy differences between planar and tetrahedral forms of a given complex in solution have been considered elsewhere.⁴ Because most of these quantities are not subject to direct experimental evaluation even in those instances where the planar \rightleftharpoons tetrahedral equilibrium exists, it is not possible now to provide a satisfactory explanation of the stereochemical patterns evident in Table IV. Any such explanation must take into account differences in ligand field stabilization energies of the two structures, among other terms. These differences cannot be meaningfully estimated due to the lack of information on the electronic structures of known planar isomers and also the spin multiplicities of the undetected planar and tetrahedral forms of Fe(II) and Cr(II), respectively. Indeed, there is no evidence at the present time that there exist for a given complex well-defined energy minima corresponding to planar and tetrahedral isomers unless the isomers have different spin multiplicities. In those cases where the intrinsic ligand field strengths are insufficient to cause a spin change in passing from one limiting structure to another, the system may respond by populating one of these structures only or by progressively, rather than discontinuously, distorting toward the other structure to an extent expected to be mainly dependent upon steric factors and temperature. The latter appears to be the case with the copper(II) salicylaldimines for which there can be no difference in spin multiplicity between limiting planar and tetrahedral geometries.

Acknowledgment.—This research was supported by the Petroleum Research Fund and the National Science Foundation under Grant GP-7576X.

(42) K. Knauer, P. Hemmerich, and J. D. W. van Voorst, *Angew. Chem. Intern. Ed. Engl.*, **6**, 262 (1967); O. Siimann and J. Fresco, *Inorg. Chem.*, **8**, 1846 (1969).