

Co-O or Cr-O bond affect the other only indirectly. This factor and the decreased overlap of the Co(III) and Cr(II) e_g orbitals *via* the carboxylate π system make the carboxylate ions less effective than halide ions in the Co(III)-Cr²⁺ reactions by a factor of about 10⁷.

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Preparation and Stereochemistry of Bis-Chelate Chromium(II), Manganese(II), Iron(II), and Cobalt(II) Complexes of the Types M-O₄ and M-O₂S₂

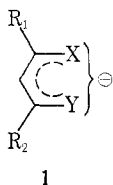
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A series of monomeric bis-chelate metal(II) complexes derived from the β -difunctional ligand **1** with X = Y = O and X = O, Y = S has been prepared and their stereochemistry has been established in the crystalline state and in solutions of noncoordinating solvents. The bis(dipivaloylmethanido) complexes Cr(dpm)₂ and Mn(dpm)₂ have been synthesized for the first time and are members of an extensive series of M(dpm)₂ complexes, M = Cr(II)-Zn(II), of known structure. Cr(dpm)₂ is shown to be planar. The monothio analogs Fe(Sdpm)₂ and Co(Sdpm)₂ have also been prepared. The former, like Fe(dpm)₂, is tetrahedral but the latter is planar in the solid and exhibits a planar \rightleftharpoons tetrahedral equilibrium in chloroform solution, in contrast to the tetrahedral and planar structures of Co(dpm)₂ and bis(dithioacetylacetonato)cobalt(II), respectively, in both phases. Several other bis(monothio- β -diketonato)cobalt(II) complexes are shown to be tetrahedral in both the solid and solution phases. Several stereochemical patterns of four-coordinate complexes which may be recognized from the results of this and other investigations are summarized.

Introduction

In the course of investigating the stereochemistry of monomeric bis-chelate metal(II) complexes, we have utilized the β -difunctional ligand **1**. The advantage of this ligand system, as emphasized previously,² lies



in the relative synthetic ease by which the donor atoms or groups X and Y and the terminal substituents R₁ and R₂ can be varied. In order to clarify certain of the factors which govern the preferential stability of the planar and tetrahedral stereoisomers, we are currently engaged in an investigation of series of bis-chelate complexes of titanium(II) through zinc(II) derived from **1**. A particular advantage of **1** is that alterations in the donor atoms X and Y are unlikely to produce significant, purely steric effects on the relative stabilities of stereoisomers of a given metal ion, with the consequence that structural differences can be related to the electronic properties of various donor-atom sets as implicated in this ligand system. Further, ligands of this type are known or are potentially able to form complexes with a variety of divalent metal ions,

thereby allowing stereochemistry to be investigated as a function of the coordinated metal ion in series of complexes possessing constant ligand structure. This report is concerned with the preparation and stereochemistry of monomeric complexes having X = Y = O and X = S, Y = O.

Bis-chelate complexes of cobalt(II), nickel(II), copper(II), and zinc(II) derived from **1** with X = Y = O have been thoroughly investigated and important information concerning their electronic and structural properties has been collected.³ These complexes, especially the acetylacetonates, are polymeric in the solid state and in solutions of noncoordinating solvents. Bulky terminal substituents tend to depress association but the only ligand which uniformly produces monomeric species is dipivaloylmethane (**1**, R₁ = R₂ = *t*-C₄H₉).⁴ Hence, the series of complexes Fe(dpm)₂,^{5,6} Co(dpm)₂,^{7,8} Ni(dpm)₂,^{9,10} Cu(dpm)₂,^{9,11} and Zn(dpm)₂⁷

(3) For a review of β -diketone complexes see J. P. Fackler, Jr., *Progr. Inorg. Chem.*, **7**, 361 (1966).

(4) The following abbreviations of the ligand anions **1** are used throughout: acac, acetylacetonate; Sacac, monothioacetylacetonate; SacSac, dithioacetylacetonate; bzac, benzoylacetonate; Sbzac, thiobenzoylacetonate; dpm, dipivaloylmethanide; Sdpm, monothiodipivaloylmethanide; Sdbm, monothiodibenzoylmethanide.

(5) J. P. Fackler, Jr., D. G. Holah, D. A. Buckingham, and J. T. Henry, *Inorg. Chem.*, **4**, 920 (1965).

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(8) F. A. Cotton and R. H. Soderberg, *ibid.*, **3**, 1 (1964).

(9) F. A. Cotton and J. J. Wise, *ibid.*, **5**, 1200 (1966).

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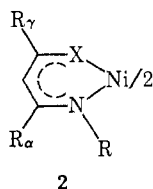
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(1) Petroleum Research Fund predoctoral fellow, 1968-1969.

(2) J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968).

is of considerable stereochemical significance for it represents one of the most extended series of bis chelates with the same ligands for which the structures of all members are known in the solid phases and in solutions of noncoordinating solvents.¹² Ni(dpm)₂ and Cu(dpm)₂ are planar and the other three complexes are tetrahedral.

The replacement of oxygen by sulfur in bis-chelate cobalt(II) and nickel(II) complexes of 1 has two important structural consequences, which, as has been pointed out recently,¹³ are depolymerization and the tendency to stabilize the planar form. Unlike Ni(acac)₂ and Co(acac)₂, which are trimeric^{10,14} and tetrameric,^{8,15} Ni-O₂S₂,¹⁶⁻¹⁸ Ni-S₄,^{17,19} and Co-S₄¹⁹ complexes are monomeric in the solid and solution phases. The tendency of sulfur donor atoms to stabilize preferentially the planar stereochemistry is illustrated by the tetrahedral and planar structures of Co(dpm)₂,^{7,8} and Co(SacSac)₂,^{19b} respectively. Further, a recent study¹⁸ of pairs of nickel(II) complexes 2 (X = O, S), whose members are identical except for the donor atoms X,



has shown that in noncoordinating solvents where the planar ⇌ tetrahedral equilibrium obtains, the population of the planar isomer of the β-aminothione complex is always considerably larger than that of the β-ketoamine member of the same pair.

Because no substantive information has been available concerning the structures of monomeric bis(β-diketonato) complexes of first-row transition metals lying to the left of cobalt, we have extended the range of known M(dpm)₂ complexes by preparing the manganese(II) and chromium(II) analogs. In a continuation of our previous work¹³ dealing with the relative stereochemical effects of oxygen and sulfur donor atoms in four-coordinate complexes, we have prepared the monothio-β-diketone complexes Fe(Sdpm)₂, Co(Sdpm)₂, Co(Sacac)₂, and Co(Sbzac)₂. This report is concerned with the syntheses of these new complexes and estab-

lishment of their structures, where possible, in the solid and solution phases. In the course of this investigation the existence of the planar ⇌ tetrahedral structural equilibrium for Co(Sdpm)₂ in solution has been established. This equilibrium, while not uncommon for bis-chelate nickel(II) complexes of diverse ligand structures, has previously been observed for cobalt(II) complexes only in a series of bis(β-ketoamine) species.²⁰

Experimental Section

Preparation of Ligands. (a) **2,2',6,6'-Tetramethyl-3,5-heptanedione.**—Dipivaloylmethane was prepared according to the procedure of Kopecky, *et al.*,²¹ bp 104–108° (35 mm); lit.²¹ bp 100–102° (36 mm).

(b) **2,2',6,6'-Tetramethyl-5-mercaptohept-4-en-2-one.**—Monothiodipivaloylmethane was obtained by a published method;²² bp 65–68° (<1 mm); lit.²² bp 50–60° (0.8 mm).

(c) **4-Mercaptopent-3-en-2-one.**—Monothioacetylacetone was prepared by the method of Mayer, *et al.*,²³ bp 61–62° (12 mm).

(d) **1-Phenyl-1-mercaptobut-2-en-3-one.**—Thiobenzoylacetone was prepared by the condensation of methylthiobenzoate and acetone in the presence of sodium hydride according to the procedure of Uhlemann and Thomas;²⁴ mp 60–61°; lit.²⁴ mp 61–62°.

Preparation of Complexes.—Most of the complexes utilized in this investigation are extremely reactive with atmospheric oxygen. Preparations and recrystallizations or sublimations were performed using glassware fitted with standard taper joints and side arms equipped with vacuum stopcocks.²⁵ The equipment was easily evacuated and the reaction mixtures, solutions, and solid complexes were exposed only to oil pump vacuum and rigorously purified nitrogen. Thoroughly dried and degassed solvents were used in all preparations. The melting points reported below were obtained in evacuated capillaries. Yields of purified complexes ranged from 20 to 60%.

(a) **Bis(dipivaloylmethanido)cobalt(II), Co(dpm)₂.**—This compound was prepared as previously described and purified by two sublimations at 137° (10⁻⁴ mm) to yield light violet crystals, mp 143–144°; lit.⁸ mp 142°.

(b) **Bis(2,2,6,6'-tetramethyl-5-mercaptohept-4-en-2-onato)cobalt(II), Co(Sdpm)₂.**—To a solution of 6.8 g (0.034 mol) of 2,2',6,6'-tetramethyl-5-mercaptohept-4-en-2-one in 20 ml of methanol was added 5.0 g (0.017 mol) of cobaltous acetate tetrahydrate dissolved in 75 ml of methanol. The reaction mixture immediately turned maroon and red crystals precipitated. After stirring for 45 min at room temperature the mixture was cooled to -20° and the crystals were collected by filtration. The product was washed twice with small portions of methanol and dried under vacuum pump pressure to yield maroon crystals, mp 143–144°. *Anal.* Calcd for C₂₂H₃₈O₂S₂Co: C, 57.74; H, 8.37; S, 14.01. Found: C, 57.69; H, 8.23; S, 13.81.

(c) **Bis(1-phenyl-1-mercaptobut-2-en-3-onato)cobalt(II), Co(Sbzac)₂.**—The preparative procedure was the same as that used for Co(Sdpm)₂. The product was obtained as red crystals, mp 193–195°. *Anal.* Calcd for C₂₀H₁₈O₂S₂Co: C, 58.10; H, 4.42. Found: C, 58.45; H, 4.42.

(d) **Bis(4-mercaptopent-3-en-2-onato)cobalt(II), Co(Sacac)₂.**—The procedure for the preparation of Co(Sdpm)₂ led to a red microcrystalline product, mp 195–196°. *Anal.* Calcd for C₁₀H₁₄O₂S₂Co: 41.52; H, 4.88; S, 22.17; Found: C, 41.75; H, 4.85; S, 22.23.

(20) (a) G. W. Everett, Jr., and R. H. Holm, *J. Am. Chem. Soc.*, **88**, 2442 (1966); (b) G. W. Everett, Jr. and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

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(18) For a brief summary of the chemistry of bis(monothio-β-diketone) complexes, see R. C. Mehrotra, V. D. Gupta, and D. Sukhani, *Inorg. Chim. Acta Rev.*, **2**, 111 (1968).

(19) (a) R. L. Martin and I. M. Stewart, *Nature*, **210**, 522 (1966); (b) R. Beckett and B. F. Hoskins, *Chem. Commun.*, 908 (1967); (c) A. Ouchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Japan*, **41**, 2004 (1968).

(e) **Bis(dipivaloylmethanido)iron(II), Fe(dpm)₂.**—This compound was obtained by a previously reported method⁵ and was purified by two sublimations at 90° (10⁻⁴ mm) to yield bright yellow crystals, mp 116–118°.

(f) **Bis(2,2'-6,6'-tetramethyl-5-mercaptohept-4-en-2-onato)iron(II), Fe(Sdpm)₂.**—A solution of 4.0 g (0.014 mol) of ferrous sulfate heptahydrate in 60 ml of water containing 1 drop of concentrated sulfuric acid was treated with a solution of 5.5 g (0.028 mol) of 2,2',6,6'-tetramethyl-5-mercaptohept-4-en-3-one in 120 ml of methanol, followed by slow addition of 1.5 g of sodium hydroxide in 80 ml of water. The addition of base produced a red precipitate. The reaction mixture was stirred for 20 min and the solid was collected by filtration and dried under pump pressure. The solid was extracted with 150 ml of cold *n*-hexane, the red solution was filtered, and the filtrate was reduced in volume to 100 ml and maintained at -78° for 2 hr. The resultant brick red crystals were filtered off and recrystallized again from *n*-hexane and then sublimed at 140° (10⁻⁴ mm). Brick red crystals were obtained; mp 130–132°. *Anal.* Calcd for C₂₂H₃₈O₂S₂Fe: C, 58.14; H, 8.43; S, 14.11. Found: C, 58.29; H, 8.41; S, 14.09.

(g) **Bis(dipivaloylmethanido)manganese(II), Mn(dpm)₂.**—This compound was prepared by a nonaqueous chelation reaction in *t*-butyl alcohol which has been described in detail elsewhere.²⁵ Bis(tetraethylammonium) dibromodichloromanganate(II) was employed as the metal ion source. The reaction mixture was worked up by evaporation of the *t*-butyl alcohol solvent and subsequent extraction of the solid residue with a mixture of toluene-*n*-heptane, 4:1 (v/v). Cooling of the filtered extract to -15° yielded a very hygroscopic fluffy yellow solid, mp 191–193°, of probable composition C₃₀H₅₈O₆NClMn. *Anal.* Calcd: C, 61.36; H, 9.96; N, 2.38. Found: C, 61.48; H, 9.78; N, 2.37. This compound, which is perhaps a five-coordinate species of the type [(C₂H₅)₄N][Mn(dpm)₂Cl], was heated in a sublimation apparatus at 180° (10⁻⁴ mm) to yield pure Mn(dpm)₂ as the sublimate and leave a solid white residue. The pure product consisted of light yellow crystals, mp 102–103°. *Anal.* Calcd for C₂₂H₃₈O₄Mn: C, 62.69; H, 9.09. Found: C, 62.62; H, 9.23.

(h) **Bis(dipivaloylmethanido)chromium(II), Cr(dpm)₂.**—The procedure employed is a modification of a nonaqueous chelation method reported previously.²⁶ A solution of 9.2 g (0.050 mol) of dipivaloylmethane in 150 ml of tetrahydrofuran freshly distilled from lithium aluminum hydride was cooled to -20° and treated dropwise with 32 ml of 1.6 *N* *n*-butyllithium (0.051 mol) in *n*-hexane. Anhydrous chromium(II) acetate (6.0 g, 0.035 mol) was introduced; the reaction mixture was allowed to warm to room temperature and then vigorously stirred for 18 hr. After removal of the solvent *in vacuo* the solid residue was extracted with boiling *n*-pentane. The filtrate of the extract solution afforded upon cooling at -78° yellow-brown crystals, which were collected by filtration and recrystallized from *n*-pentane. Golden yellow crystals were obtained; mp 193–194°. *Anal.* Calcd for C₂₂H₃₈O₄Cr: C, 63.13; H, 9.15. Found: C, 63.12; H, 9.15.

X-Ray Powder Data.—Powder photographs were obtained using a Philips Debye-Scherrer camera having a diameter of 114.6 mm. Cu K α radiation with an Ni filter was used for Cr(dpm)₂ and Cu(dpm)₂. Mn(dpm)₂ was examined by both Cu K α (Ni filter) and Mo K α (Zr filter) radiation. All samples were sealed in 0.3- or 0.5-mm diameter lead-free borosilicate capillaries. The following interplanar spacings (Å) and visually estimated relative intensities were obtained: Cr(dpm)₂ (recrystallized): 9.36 (vs), 7.80 (s), 7.15 (m), 5.84 (m), 5.47 (m), 4.91 (vs), 4.77 (m), 4.40 (m), 3.85 (vw), 3.74 (m), 3.61 (vw), 3.47 (w), 3.31 (w), 2.00 (m). Cu(dpm)₂ (recrystallized): 9.66 (vs), 7.84 (s), 7.15 (m), 5.82 (m), 5.47 (m), 4.93 (vs), 4.80 (m), 4.42 (m), 4.12 (vw), 4.02 (vw), 3.88 (w), 3.73 (m), 3.64 (vw), 3.47 (m), 3.31 (w), 2.00 (w). Mn(dpm)₂ (sublimed): 12.35 (m),

9.77 (vs), 8.99 (m), 7.89 (m), 7.44 (m), 6.73 (w), 6.29 (w), 5.30 (w), 5.01 (s), 4.49 (w), 4.09 (w), 3.79 (vw), 3.36 (vw), 2.94 (w), 2.32 (w), 2.25 (w). Zn(dpm)₂ (sublimed): 9.61 (vs), 6.25 (s), 5.34 (w), 4.82 (m), 4.68 (s), 4.45 (w), 4.01 (m), 3.59 (vw), 3.24 (m), 2.95 (vw), 2.88 (vw), 2.76 (vw), 2.63 (w), 2.58 (w), 2.49 (vw). The first two compounds are definitely isomorphous and therefore planar.⁹ Sublimed Mn(dpm)₂ displays a powder pattern dissimilar to those of Cr(dpm)₂ and Cu(dpm)₂. The interplanar spacings bear no convincing resemblance to those reported⁶ for the isomorphous tetrahedral trio of Fe(dpm)₂, Co(dpm)₂, and Zn(dpm)₂. A more complete set of spacings for Zn(dpm)₂ than that reported was calculated from the single-crystal X-ray data and further indicated the lack of isomorphism.

Physical Measurements.—Because of the extreme sensitivity of most of the complexes to oxygen, all measurements were carried out using rigorously degassed solvents under a pure nitrogen atmosphere or *in vacuo*. Magnetic measurements of solids and solutions were performed by the Gouy method using an aqueous nickel chloride solution and freshly boiled, distilled water as the respective calibrants. Magnetic measurements of certain of the cobalt(II) complexes were also made by the nmr method,²⁷ but, as discussed subsequently, this method produced inaccurate results. Electronic spectra were obtained on a Cary Model 14 spectrophotometer. Solutions were measured in 1-cm cells which could be evacuated. Mass spectra were determined using a Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 eV.

Results and Discussion

As emphasized at the outset, the ligand 1 with R₁ = R₂ = *t*-C₄H₉ has the important property of forming sterically encumbered complexes which are resistant to association, thereby permitting the study of the structures and electronic properties of discrete monomers. There is no evidence that the *t*-butyl substituents, compared to others such as methyl, for example, have any significant structural role other than suppression of oligomerization. Thus, monomeric Co(acac)₂ in inert solvents and in a carbon dioxide matrix²⁸ is tetrahedral, and Ni(acac)₂ monomer in the gas phase and inert solvents and when matrix-isolated is planar.²⁸ The analogous M(dpm)₂ complexes possess these same structures. Evidence is summarized in the following sections which bears on the solid- and solution-phase stereochemistry of a group of monomeric chromium(II), manganese(II), iron(II), and cobalt(II) complexes of the types M-O₄ and, where preparable, M-O₂S₂. Relevant magnetic and spectral data are given in Tables I and II and Figures 1–3. All complexes are unstable to oxidation, especially in solution; no attempt has been made to characterize definitely the oxidation products.

Cr(dpm)₂.—Previous attempts to prepare this compound have failed.³ By employing due precautions against oxidation it may be readily obtained by a nonaqueous chelation procedure using anhydrous chromous acetate as the metal ion source. Cr(dpm)₂ is one of the very few discrete four-coordinate chromium(II) species isolated, the only others being CrBr₂((C₆H₅)₃PO)₂ (yellow form) and CrI₂((C₆H₅)₃PO)₂.²⁹ Cr(acac)₂ has been synthesized,³⁰ but, judging from its reported

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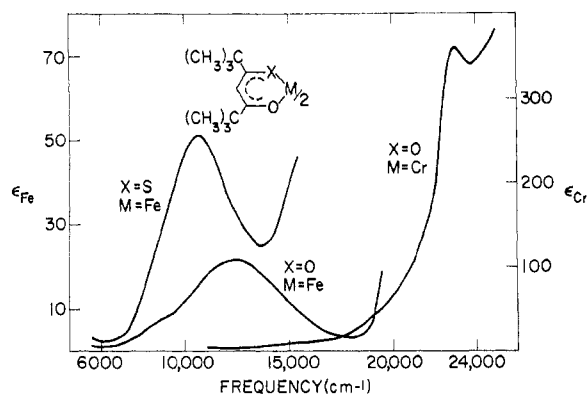


Figure 1.—Ligand field solution spectra of $\text{Cr}(\text{dpm})_2$ (toluene), $\text{Fe}(\text{dpm})_2$ (benzene), and $\text{Fe}(\text{Sdpm})_2$ (toluene) at $\sim 25^\circ$.

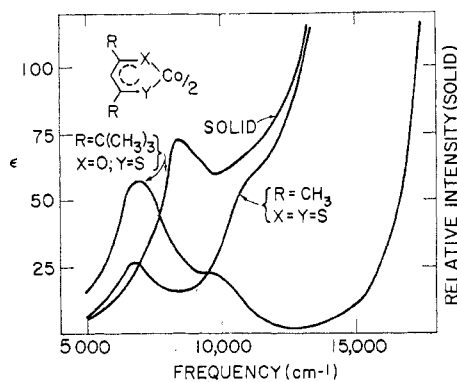


Figure 2.—Ligand field spectra of $\text{Co}(\text{Sdpm})_2$, solid and in toluene solution, and of $\text{Co}(\text{SacSac})_2$, in chloroform solution, at $\sim 25^\circ$.

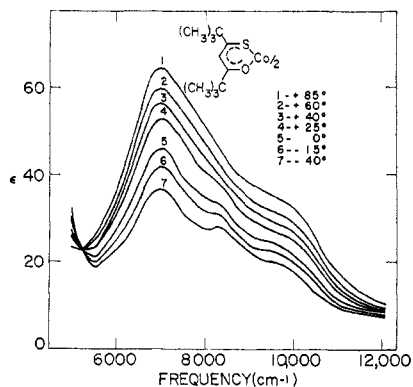


Figure 3.—Temperature dependence of the ligand field spectrum of $\text{Co}(\text{Sdpm})_2$ in toluene solution.

solubility properties, it is very likely oligomerized. $\text{Cr}(\text{bzac})_2$ has been isolated only as its dipyrindinate.³¹ $\text{Cr}(\text{dpm})_2$ has a spin-quintet ground state in toluene solution and in the crystalline state is strictly isomorphous and thus isostructural with $\text{Cu}(\text{dpm})_2$ and $\text{Ni}(\text{dpm})_2$.⁹ Its ligand field spectrum in toluene solution is shown in Figure 1 and closely resembles that measured in a hydrocarbon mull. The only well-defined feature is that at $23,000\text{ cm}^{-1}$ superimposed on a more intense band in the ultraviolet region. A very

(31) R. Nast and H. Rückemann, *Chem. Ber.*, **93**, 2329 (1960).

TABLE I
MAGNETIC MOMENTS OF $\text{Cr}(\text{II})$, $\text{Mn}(\text{II})$,
 $\text{Fe}(\text{II})$, AND $\text{Co}(\text{II})$ COMPLEXES

Complex	Solid μ_{eff} , BM	Soln			
		Solvent	Temp, $^\circ\text{C}$	Concn, mM	μ_{eff} , BM
$\text{Cr}(\text{dpm})_2$	<i>a</i>	$\text{C}_6\text{H}_6\text{CH}_3$	19	98.8	4.84
$\text{Mn}(\text{dpm})_2$	<i>a</i>	$\text{C}_6\text{H}_5\text{CH}_3$	18	58.0	5.51
$\text{Fe}(\text{dpm})_2$	5.0 ^b	$\text{C}_6\text{H}_5\text{CH}_3$	18	92.0	5.20
$\text{Fe}(\text{Sdpm})_2$	<i>a</i>	$\text{C}_6\text{H}_5\text{CH}_3$	18	65.6	5.18
$\text{Co}(\text{dpm})_2$	4.34 ^c	CHCl_3	20	80.0	4.56 ^a
$\text{Co}(\text{Sdpm})_2$	2.39	CHCl_3	21	36.9	3.17
		$\text{C}_6\text{H}_5\text{CH}_3$ ^d	17	54.9	3.22
		CHCl_3 ^e	5	29.3	3.07
		CHCl_3 ^e	25	29.3	3.35
		CHCl_3 ^e	45	29.3	3.65
$\text{Co}(\text{Sbzac})_2$	4.45	CHCl_3	20	46.2	4.28
$\text{Co}(\text{Sacac})_2$	4.59	CHCl_3	21	82.6	4.41
$\text{Co}(\text{SacSac})_2$	2.29 ^f	<i>g</i>			

^a Not measured. ^b References 5 and 6. ^c Reference 8. ^d 15% v/v TMS- $\text{C}_6\text{H}_5\text{CH}_3$. ^e 10% v/v cyclohexane- CHCl_3 . ^f 2.0 BM.^{19a} ^g Insufficiently soluble for accurate measurement. ^h 4.13 BM (benzene solution) reported in ref 8. The source of the disagreement is undoubtedly partial oxidation, which was known to occur during earlier measurements.⁸

TABLE II
LIGAND FIELD SPECTRAL DATA FOR
 $\text{Cr}(\text{II})$, $\text{Fe}(\text{II})$, AND $\text{Co}(\text{II})$ COMPLEXES

Complex	Medium	λ_{max} , cm^{-1}	ϵ , l. mol ⁻¹ cm ⁻¹ ^a
$\text{Cr}(\text{dpm})_2$	Toluene	$\sim 16,500$ sh, 23,000	$\sim 12, 360$
	Mull	23,000	...
$\text{Fe}(\text{dpm})_2$	Benzene	~ 9000 (sh), 12,400	$\sim 8, 22$
	Mull	11,500	...
$\text{Fe}(\text{Sdpm})_2$	Toluene	10,700	51
	Mull	10,500	...
$\text{Co}(\text{dpm})_2$ ^b	C_6H_6	7000, $\sim 10,000$ sh, 18,000	45, $\sim 15, 40$
$\text{Co}(\text{Sdpm})_2$ ^c	Toluene	7100, ~ 9500 sh	64, ~ 35
	Mull	8300	...
$\text{Co}(\text{Sacac})_2$	Chloroform	7300, ~ 9500 sh	25, ~ 50
$\text{Co}(\text{Sbzac})_2$	Chloroform	7200, ~ 9500 sh	92, ~ 54
$\text{Co}(\text{SacSac})_2$ ^d	Chloroform	6800, $\sim 10,900$ sh	26, ~ 56

^a Uncorrected for underlying absorption. ^b Data from ref 8; spectrum of solid compound the same. ^c 85° (see Figure 3). ^d For more complete data see ref 19a.

weak band ($\epsilon \sim 12$) is observed at *ca.* $16,000\text{ cm}^{-1}$. This spectrum bears no relation to those of the CrX_2 - $((\text{C}_6\text{H}_5)_3\text{PO})_2$ complexes mentioned above and CrCl_4^{2-} (in KCl-LiCl eutectic),³² for which distorted tetrahedral structures have been proposed. These species show a single ligand field band at *ca.* $10,000\text{ cm}^{-1}$ assigned as ${}^3\text{T}_2 \rightarrow {}^5\text{E}$ in idealized tetrahedral symmetry. From these observations it is concluded that $\text{Cr}(\text{dpm})_2$ is planar in the solid and solution phases. Attempts to prepare $\text{Cr}(\text{Sdpm})_2$ by several different methods yielded a dark oily product which could not be crystallized.

Mn(dpm)₂.—A previously attempted synthesis of this compound in aqueous acetone is reported to yield the dihydrate.³³ The anhydrous compound has been obtained in this work by a nonaqueous chelation reaction. Its magnetic moment of 5.51 BM in toluene solution

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(33) A. L. Shugarman, *Dissertation Abstr.*, **29B**, 925 (1965).

suggests the anticipated spin-sextet ground state consistent with a tetrahedral or weak-field planar structure. This value is less than the spin-only value of 5.9 BM and, although reproducible to ± 0.05 BM using independently prepared solutions, may be due to partial oxidation. Sublimed $\text{Mn}(\text{dpm})_2$ does not appear to be isomorphous with either planar or tetrahedral $\text{M}(\text{dpm})_2$ complexes, and among the known complexes of this type it is the only one not possessing an obvious isomorphous relationship. In view of this result further conformation of composition was sought by mass spectrometry. The 70-eV spectrum revealed the parent ion $^{55}\text{Mn}(\text{dpm})_2^+$ (m/e 412) as the most intense peak, no peaks of higher mass number, and a fragmentation pattern entirely consistent with that observed for pure $\text{Co}(\text{dpm})_2$. Attempts to observe the ligand field spectrum in concentrated toluene solution led to the detection of a single feature at $17,900\text{ cm}^{-1}$ ($\epsilon \sim 3$). No definite evidence for the structure of $\text{Mn}(\text{dpm})_2$ can be offered, but because of the general similarities in the structural chemistry of manganese(II) and zinc(II) complexes, it is considered likely that this compound, like $\text{Zn}(\text{dpm})_2$, is tetrahedral. No structural information on $\text{Mn}(\text{acac})_2$ or other bis(β -diketonato)manganese(II) compounds is available; the former is claimed to be trimeric in nonpolar solvents.³⁴ We were unable to prepare a pure sample of $\text{Mn}(\text{Sdpm})_2$.

Fe(dpm)₂ and Fe(Spdm)₂.—Previous work has established that $\text{Fe}(\text{dpm})_2$ in the solid state is tetrahedral by virtue of its isomorphism with $\text{Co}(\text{dpm})_2$ and $\text{Zn}(\text{dpm})_2$ and that it is monomeric in benzene solution.^{5,6} Its magnetic moment in toluene solution is unimportantly different from that reported for the solid and is not structurally diagnostic, particularly in view of the high-spin moment (5.12 BM) of iron(II) in the only established planar $\text{Fe}-\text{O}_4$ coordination unit, provided in gillespites, $\text{BaFeSi}_4\text{O}_{10}$.³⁵ Although it was reported earlier that no ligand field transitions of $\text{Fe}(\text{dpm})_2$ could be observed,⁶ we have found in benzene solution a very weak shoulder at $\sim 9000\text{ cm}^{-1}$ and a maximum at $12,400\text{ cm}^{-1}$. The spectrum of the solid is unquestionably similar to that of the solution but less well resolved. A definite peak at $11,500\text{ cm}^{-1}$ is observable but the low-energy shoulder could not be detected. These absorption features are presumably derived from the $^5\text{E} \rightarrow ^5\text{T}_2$ transition in T_d symmetry which is apparently split by the actual symmetry (D_{2d} or lower) of the complex. If this assignment is correct, Δ_t may be roughly estimated as *ca.* $10,000$ – $12,000\text{ cm}^{-1}$ indicating that dpm^- generates a much stronger ligand field than do chloride, oxide, and other common ligands in their tetrahedral iron(II) complexes for which Δ_t falls in the 3000 – 6000-cm^{-1} range.³⁶ Relatively strong ligand fields ($\Delta_t \approx 11,000$ – $12,500\text{ cm}^{-1}$)

have also been observed in a series of bis(β -ketoamino)-iron(II) complexes, $\text{Fe}[\text{R}_7\text{COCHC}(\text{NR})\text{R}_a]_2$, whose large R groups ensure a tetrahedral structure.³⁷ Replacement of two oxygen donor atoms by sulfur does not result in any stereochemical changes, in contrast to the results obtained with $\text{Co}(\text{Sdpm})_2$ (*vide infra*) and the nickel(II) complexes 2. The magnetic and spectral properties of $\text{Fe}(\text{Sdpm})_2$ are convincingly similar to those of $\text{Fe}(\text{dpm})_2$, and, accordingly, the former is assigned a tetrahedral structure.

Co(dpm)₂, Co(Spdm)₂, and Related Complexes.—Upon noting that $\text{Co}(\text{dpm})_2$ ^{7,8} and $\text{Co}(\text{SacSac})_2$ ^{19a,b} are tetrahedral and planar, respectively, in the solid and in solution, we became interested in the stereochemical properties of cobalt(II) complexes containing the mixed donor atom set O_2S_2 . Previously, definite characterization data had been reported only for $\text{Co}(\text{Sdbm})_2$.³⁸ A brief report indicates that $\text{Co}(\text{Sacac})_2$ has been prepared³⁹ but no physical properties were described. We have prepared the series of complexes $\text{Co}(\text{Sdpm})_2$, $\text{Co}(\text{Sacac})_2$, and $\text{Co}(\text{Sbzac})_2$. The moments of the latter two complexes in the solid state indicate that they are tetrahedral. $\text{Co}(\text{Sdpm})_2$, on the other hand, has a doublet ground state in the solid as does $\text{Co}(\text{SacSac})_2$. The absorption spectra of crystalline $\text{Co}(\text{Spdm})_2$ and $\text{Co}(\text{SacSac})_2$ in chloroform solution (*cf.* Figure 2) are similar and the features at 8300 and 6800 cm^{-1} , respectively, correlate with the 8300 – 8600-cm^{-1} bands observed for a series of low-spin bis(β -ketoamino)cobalt(II) complexes with $\text{X} = \text{O}$, $\text{Y} = \text{NH}$.²⁰ No definite assignment is yet possible for these absorptions, but they are obviously characteristic of a planar structure.

Upon dissolution in chloroform or toluene, the magnetic moment of $\text{Co}(\text{Sdpm})_2$ undergoes a marked increase. Further, as the data in Table I reveal, the moment in chloroform solution is markedly temperature dependent in the 5 – 45° range. Associated with the rise in magnetic moment with increasing temperature are progressive spectral changes shown in Figure 3. These spectra, which were recorded in toluene solution in order to obtain a wide temperature variation, reveal a smooth change toward the typical tetrahedral spectrum of $\text{Co}(\text{dpm})_2$ ⁸ as the temperature is increased and a clear isosbestic point at 5200 cm^{-1} . The main feature at 7100 cm^{-1} increases in intensity, as does the shoulder at *ca.* 9500 cm^{-1} , while the absorption at 8300 cm^{-1} , observable as a definite peak at -40° , becomes less intense and is barely discernible in the 85° spectrum. The spectrum at this temperature

(37) D. H. Gerlach and R. H. Holm, results to be submitted for publication. These results offer further support for the assignment of absorption features of $\text{Fe}(\text{dpm})_2$ shown in Figure 1 to ligand field transitions. In addition, it is to be noted that the monomolecularity of the complex has been demonstrated in the same solvent used for the spectral measurement under conditions of higher concentration and lower temperature than those employed in that measurement. This point is made inasmuch as $\text{Fe}(\text{acac})_2$ polymer species develop a peak at $12,100\text{ cm}^{-1}$ in benzene solution,⁸ which is remarkably close in energy to the absorptions of $\text{Fe}(\text{dpm})_2$. The latter are completely removed upon brief exposure of the solution to air, indicating that they are not due to oxidized or oxygenated species.

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(39) W. I. Stephen, I. J. Thomson, and P. C. Uden, *Chem. Commun.*, 269 (1969).

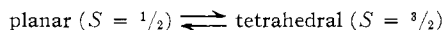
(34) D. P. Graddon and G. M. Moekler, *Australian J. Chem.*, **17**, 1119 (1964).

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

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closely resembles those of $\text{Co}(\text{Sacac})_2$ and $\text{Co}(\text{Sbzac})_2$ at ambient temperature in chloroform solution (*cf.* Table II) where their magnetic moments, when compared to those of the solids, indicate complete or nearly complete population of the tetrahedral isomer. The monomeric nature of this pair of complexes was confirmed by their adherence to Beer's law in chloroform solution in the 0.003–0.018 M concentration range. All magnetic and spectral changes of $\text{Co}(\text{Sdpm})_2$ were reversible with temperature.

The solution properties of $\text{Co}(\text{Spdm})_2$ are consistent only with the equilibrium



Using the relations given previously²⁰ and taking the limiting magnetic moments of the planar and tetrahedral stereoisomers as 2.39 and 4.59 BM, respectively, the thermodynamic parameters characterizing the equilibrium have been estimated from the temperature dependence of the moment of the equilibrium mixture of isomers. Using the data in Table I for a chloroform solution, ΔG values determined at the three temperatures vary linearly with temperature. These results have been obtained: $\Delta H = 4.8$ kcal/mol, $\Delta S = 15$ eu, $\Delta G_{298} = +0.33$ kcal/mol, and $N_{t,298}$ (mole fraction of tetrahedral isomer) = 0.37. Attempts to secure thermodynamic data based on magnetic moment measurements by the nmr method²⁷ over a much wider temperature range, as has been done in past studies of the structural equilibrium of bis(β -ketoamino)cobalt(II) complexes,²⁰ were not successful because of the incorrect moments yielded by this method.⁴⁰ Pmr isotropic shift studies of the structural equilibrium of $\text{Co}(\text{Sdpm})_2$ and other bis-chelate Co(II) complexes and the dynamics of configurational interchange are currently being carried out.⁴¹

Stereochemical Patterns.—The results obtained in this work together with those in the literature pre-

(40) The following results are to be compared with the appropriate data in Table I: in 10% v/v cyclohexane- CHCl_3 , $\text{Co}(\text{dpm})_2$, 4.98 BM (31°), $\text{Co}(\text{Sdpm})_2$, 3.60 BM (32°); in 15% v/v TMS-toluene, $\text{Co}(\text{Sdpm})_2$, 3.70 BM (25°); in 15% v/v TMS- CHCl_3 , $\text{Co}(\text{Sbzac})_2$, 4.60 BM (30°). Measurements were made using the TMS or cyclohexane signals. The use of the chloroform or toluene signals results in an even larger discrepancy; for example, the apparent moment of $\text{Co}(\text{dpm})_2$ obtained in this way is 5.31 BM. We have previously pointed out that use of chloroform signals in measuring moments of tetrahedral cobalt(II) complexes led to erroneously high results, but TMS signals gave results in good agreement with Gouy measurements.²⁰ With the present group of complexes signals developed by TMS and cyclohexane internal references also give apparent moments which are too high but disagree with Gouy results to a smaller extent than results calculated from solvent shifts. The source of the error must clearly be specific interactions between the complexes and the solvent and reference molecules, which might be manifested in the form of dipolar shifts of the latter arising from the magnetic anisotropies of the complexes.²⁰ This matter is being further investigated. It is noted that the moment of tetrahedral $\text{Co}(\text{S-PF}_2)_2$ measured by the nmr method is 1 BM higher than that obtained by a Gouy measurement: F. N. Tebbe, H. W. Roesky, W. C. Rode, and E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 3578 (1968).

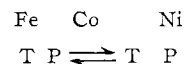
(41) D. H. Gerlach, L. H. Pignolet, and R. H. Holm, work in progress.

viously cited allow recognition of certain fundamental structural variations in four-coordinate stereochemistry, which, while obtained for complexes derived from **1**, may be of general consequence. The information summarized refers to stereochemistry in weakly interacting or noncoordinating solvents at or near room temperature (P = planar, T = tetrahedral).

(i) **Stereochemical Variation in Series of Constant Ligand Structure.**—The $\text{M}(\text{dpm})_2$ series is presently the most extensive known. Exactly the same pattern

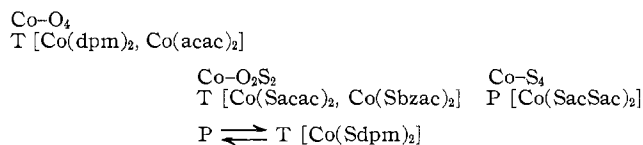
Cr	Mn	Fe	Co	Ni	Cu	Zn
P	T(?)	T	T	P	P	T

has been found in the series $\text{M}[\text{H}_2\text{B}(\text{pz})_2]_2$, $\text{M} = \text{Mn}(\text{II})$ – $\text{Zn}(\text{II})$,¹² and $\text{M}[\text{R}_\gamma\text{COCHC}(\text{NCH}_3)\text{R}_\alpha]_2$, $\text{M} = \text{Cr}(\text{II})$, $\text{Fe}(\text{II})$ – $\text{Zn}(\text{II})$.³⁷ For the $\text{M}(\text{Sdpm})_2$ series, which is more limited, a somewhat similar pattern prevails but measurable population of the planar isomer extends to



cobalt(II). The complexes $\text{M}[\text{R}_\gamma\text{COCHC}(\text{NH})\text{R}_\alpha]_2$, $\text{M} = \text{Fe}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, display the same structural trends.^{20,37}

(ii) **Stereochemical Variations in Series Having Constant Metal Ion and Varying Donor-Atom Sets.**—Restricting attention to oxygen-sulfur donor sets, stereochemical variations have thus far been observed only for cobalt(II) complexes. It is clear that replacement of oxygen by sulfur enhances the relative



stability of the planar isomer, an effect which extends to the nickel complexes **2** of the types $\text{NiO}_2(\text{NR})_2$ and $\text{NiS}_2(\text{NR})_2$.¹³ Attempts to enlarge our study of the relative stereochemical effects of oxygen and sulfur donors by examination of the series Fe-O_4 , $\text{Fe-O}_2\text{S}_2$, Fe-S_4 have thus far been thwarted by our inability to repeat the claimed preparation of $\text{Fe}(\text{SacSac})_2$,⁴² which is the only reported Fe-S_4 complex derived from **1**.

The factors responsible for the stereochemical trends in these and other series of bis-chelate metal(II) complexes will be considered in a subsequent report.³⁷

Acknowledgment.—This research was supported by the National Science Foundation under Grant GP-7576X. We thank J. G. Gordon, II, for a sample of monothioacetylacetone.

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