about 15 hr. The addition of 5.0 ml. of pentane to the reaction mixture completed the precipitation of the product. The nearly colorless solid was separated by centrifuging and dried *in vacuo*. The compound was purified by dissolving it in 50 ml. of boiling chloroform, filtering, and concentrating to about 30 ml. and then adding 100 ml. of ether. The compound soon crystallized. Another crystallization by the same procedure gave 0.5 g. of very pale yellow needles with the properties given in Table I.

Methylrhodium Chloroiodocarbonylbis(tri-*n*-butylphosphine). ---A solution of 3.0 g. of RhCl(CO)[P(*n*-C₄H₉)₃]₂ in 3.0 ml. of methyl iodide under nitrogen in a capped tube was allowed to react for 15 hr. at room temperature. The excess methyl iodide was evaporated *in vacuo* and the residue was recrystallized first from pentane containing a little ether with cooling to -80° , then from hexane with cooling to 0°. There was obtained 2.43 g. of pale yellow prisms. Another crystallization from pentane with cooling to -80° gave the samples whose properties are reported in Table I.

Acetylrhodium Chloroiodocarbonylbis(tri-n-butylphosphine). -A solution of 1.0 g. of CH₃RhClI(CO)[$P(n-C_4H_9)_3$]₂ in 10 ml. of purified tetrahydrofuran was stirred magnetically in a 30° bath under 1 atm. of carbon monoxide until gas absorption stopped. A total of 45.0 ml, of gas was absorbed in about 48 hr, and the reaction stopped. The solvent was then removed in vacuo at 30° and the dark residue was extracted with warm methanol. The methanol solution was decanted from a dark oil which separated first. On cooling, orange crystals separated from the methanol solution. Another crystallization from methanol and one from pentane gave about 0.2 g. of material with the properties listed in Table I. The reaction was also carried out under 30 p.s.i. of CO and in methylene chloride, instead of in tetrahydrofuran, but the gas volume change could not be accurately measured because of the high vapor pressure of the methylene chloride at 30°.

Rhodium Trichlorocarbonylbis(triethylphosphine).—A solution of 1.0 g. of RhCl(CO)[P(C₂H₅)₃]₂ in 5.0 ml. of carbon tetrachloride was allowed to react at room temperature for 15 hr. in a capped tube under nitrogen. The infrared spectrum showed that the starting compound had completely reacted by then. Evaporation of the unreacted carbon tetrachloride at room temperature left a partially crystalline residue. Addition of pentane caused complete crystallization of the residue. Then crystallization from ether with cooling to -80° gave 0.2 g. of bright yellow prisms with the properties indicated in Table I.

Methyl trichloroacetate reacted with $RhCl(CO)[P(C_2H_5)_3]_2$ in a completely analogous way to give the same product. The fate of the methyl trichloroacetate or of the carbon tetrachloride in the above reaction was not determined.

Rhodium Chlorodibromocarbonylbis(tri-*n*-butylphosphine).— In a capped tube under nitrogen, 0.5 g. of RhCl(CO)[P(n-C₄H₉)₃]₂ was dissolved in 2.0 ml. of methylene chloride. A solution of 2.0 g. of bromine in 2 ml. of methylene chloride was injected. After reacting for 1 hr., the solvent was evaporated and pentane and a little ether were added to dissolve the product. On cooling to -80° , the product crystallized. Recrystallization, three times from methanol, yielded 0.3 g. of orange prisms. The properties are given in Table I.

Rhodium Chlorodiiodocarbonylbis(tri-*n*-butylphosphine).—A solution of 0.5 g. of RhCl(CO)[P(n-C₄H₉)₃]₂ in 2 ml. of ether was treated with a solution of 0.3 g. of iodine in 2 ml. of ether under nitrogen. After standing overnight, the solvent was removed *in vacuo* and the product was recrystallized three times from an ether-pentane solution with cooling to -80° . There was obtained 0.48 g. of red-brown crystals with the properties shown in Table I.

Infrared Spectra.—All infrared spectra were taken on a Perkin-Elmer Model 237B Grating Infracord. Each spectrum was calibrated with a polystyrene film and the readings reported should therefore be accurate to ± 5.0 cm.⁻¹.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Synthetic and Electron Spin Resonance Studies of Six-Coordinate Complexes Related by Electron-Transfer Reactions

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A new series of six-coordinate complexes of the general type $[MS_8C_6R_6]^z$ with $R = CF_3$ (M = Cr, Mo, W, z = 0, -1, -2) and R = CN (M = Cr, V, z = -2; M = Cr; z = -3) has been prepared. These complexes are similar to related bis complexes¹⁻⁴ in that they contain metals stabilized in several different oxidation states and complexes of given R and M can be interconverted by simple oxidation-reduction reactions. The syntheses of all compounds are described in detail, and chemical stabilities are discussed in terms of polarographic half-wave potentials. The results of magnetic susceptibility, electron spin resonance, and infrared studies are discussed. Electron spin resonance results show the presence of a strong trigonal component in the octahedral ligand field in complexes with a doublet ground state, and are not in agreement with the conventional d_0^1 or $(a_i^*)^1$ ground state. Probable electronic structures of these complexes are discussed.

Introduction

In a continuing series of investigations being carried out in these laboratories, the synthesis and characterization of a large number of four-coordinate complexes of the transition elements in which the metal is coordinated only by sulfur have been achieved.¹⁻⁴ These complexes are of the general formulation [MS₄-C₄R₄]^{*t*} in which the metal is coordinated by the bidentate *cis*-1,2-disubstituted ethylene-1,2-dithiolato group R₂C₂S₂, in which R = CF₃, CN, C₆H₅. One of the

(1) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, J. Am. Chem. Soc., 85, 2029 (1963).

(2) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, Inorg. Chem., 2, 1227 (1963).

(3) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, J. Am. Chem. Soc., 85, 3049 (1963).

(4) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, Inorg. Chem., **3**, 814 (1964).

most significant results of these investigations is the discovery that these planar complexes undergo reversible and unusually facile electron-transfer reactions which have permitted the synthesis of a wide variety of complexes with total charge z = 0, -1, -2. These complexes have been investigated by several physical methods including electron spin resonance and the probable electronic structures of several complexes with z = -1, -2 have been discussed.²⁻⁴

The existence of electron-transfer reactions in the four-coordinate series of complexes suggested that a similar set of reactions might exist among six-coordinate tris complexes of the type $[MS_6C_6R_6]^2$. The recent synthesis of $[MoS_6C_6(CF_3)_6]$ by King⁵ is especially pertinent in view of the early isolation in the

(5) R. B. King, ibid., 2, 641 (1963).

present study of salts of the anion $[CrS_6C_6(CN)_6]^{-3}$. If the chelate ring substituents are excluded, it is apparent that these two complexes differ by three valence electrons. The ready isolation and considerable stability of both complexes raised the possibility that the complexes $[MS_6C_6(CF_3)_6]$ might be reducible, and the complexes $[MS_6C_6(CN)_6]^{-3}$ oxidizable, in a series of one-electron-transfer reactions. This possibility has been investigated in the present work and the following complexes synthesized: $R = CF_3$, M =Cr, Mo, W, z = 0, -1, -2; R = CN, M = Cr, z = -2, -3, M = V, z = -2. Herein we report the syntheses of these compounds together with the results of electron spin resonance, magnetic susceptibility, and infrared spectral studies.

Experimental

Preparation of Compounds.—Disodium *cis*-1,2-dicyanoethylene-1,2-dithiolate, Na₂S₂C₂(CN)₂, was prepared by the method of Bähr and Schleitzer.⁶ Bis(trifluoromethyl)-1,2-dithietene was obtained by the gas-phase reaction of sulfur and hexafluorobutyne-2⁷ and the fraction boiling between 96 and 98° was used in the following preparations. The compound was freshly distilled before use. Tris(*cis*-1,2-ditrifluoromethylethylene-1,2dithiolato)molybdenum, [MoS₆C₆(CF₃)₆], was prepared in 60% yield using a modification of the procedure outlined by King.⁶ All melting points are uncorrected.

 $[CrS_6C_6(CF_3)_6]$.— $Cr(CO)_6$ (2.20 g.) and $(CF_3)_2C_2S_2$ (6.78 g.) were refluxed in ethylcyclohexane (100 ml.) under a nitrogen atmosphere. During the first 30 min. there was rapid evolution of carbon monoxide and the solution became intense red-purple. After 4.5 hr. the mixture was allowed to cool slowly to $\sim 50^{\circ}$; at this point evolution of gas had almost ceased and further refluxing caused marked decomposition of the product. The brownish purple solution was filtered through a sintered glass funnel and the product washed with cold 25-ml. portions of npentane until the washings were pale pink. The lustrous black crystals (5 g., 68%), which have a golden green sheen, were found to be pure enough for the subsequent preparations. The product is very sparingly soluble without reduction in dry n-pentane and CH₂Cl₂ giving a red-purple solution. An analytical sample was obtained by Soxhlet extraction using *n*-pentane as solvent, m.p. 210-215° (sealed tube) with decomposition. The reaction when carried out in methylcyclohexane for 70 hr. afforded a 55%yield. Anal. Calcd.: C, 19.73; H, 0.00; S, 26.34; F, 46.81. Found: C, 19.53; H, 0.07; S, 25.98; F, 46.44.

 $[WS_6C_6(CF_3)_6]$.—This complex was obtained by a procedure similar to that for the preparation of $[CrS_6C_6(CF_3)_6]$. However, much longer reaction times were required. In ethylcyclohexane a reflux time of 72 hr. afforded a 36% yield; in *n*-octane a reflux time of 3 weeks was necessary to produce the same yield. The product consists of lustrous black crystals having a pronounced golden green sheen. No definite melting point (sealed tube) was observed and sublimation begins at ~235°. The compound is sparingly soluble without reduction in dry nonpolar solvents giving purple-red solutions. *Anal.* Calcd.: C, 16.71; H, 0.00; S, 22.31; F, 39.66. Found: C, 16.56; H, 0.06; S, 22.99; F, 40.06.

 $[(C_6H_5)_4As]_2[MoS_6C_6(CF_3)_6]. \rightarrow A \text{ suspension of } 3.87 \text{ g. of } [MoS_6C_6(CF_3)_6] in 100 \text{ ml. of ethanol was treated with 10 ml. of hydrazine-ethanol (10\% v./v.). There was immediate evolution of nitrogen and the solution became intensly blue. The product precipitated immediately upon the addition of tetraphenylarsonium chloride (4.25 g. in 30 ml. of ethanol) as small bright blue needles. These were collected and washed with two 10-ml. portions of cold ethanol. Recrystallization from acetone-isobutyl alcohol followed by washing with isobutyl alcohol and n-pentane and drying in air gave 6.55 g. (85%) of dark blue needles, m.p. >250°. Anal. Calcd.: C, 46.77; H, 2.62; S, 12.49; F, 22.20. Found: C, 46.56; H, 2.62; S, 12.28; F, 22.15.$

 $[(C_6H_5)_4As]_2[WS_6C_6(CF_3)_6]$.—A preparation exactly the same as that for the analogous molybdenum complex gave the product

as shiny red-purple needles in 75% yield, m.p. $>250^{\circ}$. Anal. Calcd.: C, 44.24; H, 2.48; S, 11.81; F, 20.99. Found: C, 44.27; H, 2.60; S, 12.04; F, 20.73. The molybdenum and tungsten salts are readily soluble in acetone, DMF, and dichloromethane, giving intense blue and reddish purple solutions, respectively.

 $[(C_6H_3)_4As]_2[CrS_6C_6(CF_3)_6]$.—The reduction of $[CrS_6C_6(CF_3)_6]$ was performed in exactly the same manner as in the preparation of the molybdenum and tungsten dianions. In this case the product is readily soluble in ethanol, and was isolated by dropwise addition of water to the dark green alcohol solution until incipient crystallization occurred. The mixture was then cooled in ice and agitated to precipitate the product as an olive-green solid. The product was isolated, washed with 1:1 aqueous ethanol, and twice recrystallized from acetone-isobutyl alcohol to give shiny black needles in 41% yield, m.p. 193–194° dec. *Anal.* Calcd.: C, 48.13; H, 2.69; S, 12.85; F, 22.84. Found: C, 48.10; H, 2.67; S, 12.87; F, 22.91.

 $[(C_8H_5)_4As][CrS_6C_6(CF_3)_6]$.—A mixture of 0.75 g. of $[CrS_6-C_6(CF_3)_6]$ and 1.45 g. of $[(C_6H_5)_4As]_2[CrS_6C_6(CF_3)_6]$ in 100 ml. of dichloromethane (dried over molecular sieves) was refluxed for 3 hr. with the exclusion of atmospheric moisture. The dark green solution was filtered from a small amount of unreacted $[CrS_6C_6(CF_3)_6]$ (~10–20 mg.) and concentrated to 30 ml. on a vacuum line. Slow addition of 100 ml. of *n*-pentane (dried over molecular sieves) caused the product to crystallize. Filtration followed by washing with two 20-ml. portions of dry *n*-pentane and drying in a desiccator over phosphorus pentoxide gave 1.95 g. (90%) of shiny black crystals, m.p. 127.5–129°. *Anal.* Calcd.: C, 38.82; H, 1.81; S, 17.27; F, 30.70. Found: C, 38.64; H, 1.74; S, 17.43; F, 30.49.

The analogous molybdenum and tungsten complexes were prepared by an exactly similar procedure.

 $[(C_6H_5)_4A_8][MoS_6C_6(CF_3)_6]$.—The product was obtained in 91% yield as dark blue crystals, m.p. 189–192.5°. Anal. Calcd.: C, 37.35; H, 1.74; S, 16.62; F, 29.54. Found: C, 37.27; H, 1.76; S, 16.40; F, 29.24.

 $[(C_6H_5)_4As][WS_6C_6(CF_3)_6]$.—The product was obtained in 94% yield as very dark blue (almost black) crystals, m.p. 177.5–181°. Anal. Calcd.: C, 34.71; H, 1.62; S, 15.44; F, 27.45. Found: C, 34.93; H, 1.71; S, 15.14; F, 27.75.

The complexes $[(C_6H_5)_4As][MS_6C_6(CF_3)_6]$ (M = Cr, Mo, W) are sparingly soluble $(\sim 10^{-3} M)$ without decomposition in dry benzene and carbon tetrachloride, and are readily soluble in dry dichloromethane. Treatment with basic solvents such as acetone, DMF, and water causes slow reduction to the dianion. For optimum yields in the above preparations all solvents must be carefully dried.

 $[(C_8H_5)_4As]_8[CrS_6C_6(CN)_6]$.—CrCrl₃·6H₂O (2.67 g.) was dissolved in 60 ml. of distilled water and this solution was added to a solution of 5.70 g. of Na₂S₂C₂(CN)₂ in 150 ml. of distilled water. The resultant solution was heated 15 min. on a steam bath during which time an intense brown color developed. Addition of 12.7 g. of tetraphenylarsonium chloride in 100 ml. of 95% ethanol produced immediate separation of a brown oily solid which 'rapidly solidified. The crude product was dissolved in the minimum volume of hot DMF and crystallization was effected by adding water dropwise to the hot solution. The product crystallized as small light brown needles which were collected and recrystallized by the same procedure to give 11.30 g. (70%) of product, m.p. 239–244° dec. Anal. Calcd.: C, 62.18; H, 3.73; N, 5.18; S, 11.86. Found: C, 62.28; H, 3.68; N, 5.27; S, 11.82.

 $[(C_6H_5)_4As]_2[CrS_6C_6(CN)_6]$.— $[(C_6H_5)_4As]_3[CrS_6C_6(CN)_6]$ (5.41 g.) and $[MoS_6C_6(CF_3)_6]$ (2.60 g.) were refluxed together in 600 ml. of dry dichloromethane for 5 hr. The volume was reduced by distillation of 400 ml. of solvent; then 600 ml. of dry benzene was added slowly. The product which crystallized on standing was collected, washed with benzene until the washings were colorless, washed with 25 ml. of *n*-pentane, and air-dried to give 3.65 g. (89%) of shiny black crystals, m.p. 225–230° dec. *Anal.* Calcd.: C, 58.15; H, 3.25; N, 6.78; S, 15.53. Found: C, 57.52; H, 3.33; N, 6.58; S, 15.40.

 $[(C_6H_5)_4AS]_2[VS_6C_6(CN)_6]$.—Anhydrous vanadium trichloride (1.90 g.) was added to a suspension of 7.0 g. of Na₂S₂C₂(CN)₂ in 150 ml. of dry freshly distilled tetrahydrofuran. On shaking for 20 min. the suspended solids dissolved to give a dark green solution. The solution was filtered and added to a solution of 15.0 g. of tetraphenylarsonium chloride in 150 ml. of ethanol. The solid which immediately precipitated was collected, washed

⁽⁶⁾ G. Bähr and G. Schleitzer, Ber., 90, 438 (1957).

⁽⁷⁾ C. G. Krespan, J. Am. Chem. Soc., 83, 3434 (1961).

with ethanol, and then treated with 500 ml. of acetone. To the clear dark green acetone filtrate water was added slowly until incipient crystallization. The shiny black crystals isolated were washed with absolute ethanol and air-dried to yield 8.3 g. (55%). Anal. Calcd.: C, 58.20; H, 3.26; N, 6.79; S, 15.54. Found: C, 58.32; H, 3.41; N, 6.75; S, 15.67.

Physical Measurements.—Measurements of magnetic susceptibilities, electron spin resonance, conductivities, infrared and electronic spectra, and polarographic half-wave potentials were all made as previously described.²

Results and Discussion

The complexes which are the subjects of this investigation are of the general type 1. All complexes synthesized in this work are listed in Table I together with



results of conductivity and magnetic susceptibility measurements. Inspection of the table reveals that three isoelectronic series of complexes have been prepared. These series are summarized as follows: series I, (Cr, Mo, W)⁰ (R = CF₃); series II, (V)⁻² (R = CN), (Cr, Mo, W)⁻ (R = CF₃); series III, (Cr)⁻² $(R\ =\ CN),\ (Cr,\ Mo,\ W)^{-2}\ (R\ =\ CF_3).$ In addition, the existence of the following species is implied by the polarographic half-wave potential measurements given in Table II: $(V)^-$ (R = CN), (Cr)^- (R = CN), $(V)^{-3}$ (R = CN). None of these species has been isolated in the present investigation. As will become apparent in the following discussion, a number of complexes, especially those with $R = CF_3$, display a range of oxidative stability such that they can be interconverted among these three series by simple oxidationreduction reactions.

TABLE I

Conductivity and Magnetic Susceptibility Data^a

\mathbf{v}_p	$10^{6} \chi^{M}_{cor}$	µ _{eff} , B.M. [⊄]
	Dia.d	• •
56	1508	1.89
139	3638	2.95
136	3499	2.89
208	6374	3.90
	d	
54	1336	1.79
133	d	
	d	
60	1315	1.77
134	d	
140	1398	1.82
		$\begin{array}{cccccccc} {}^{Ab} & 10^{e} {}^{M} {}^{e} {}^{c} {}^{o} {}^{r} \\ \hline & & {\rm Dia.}^{d} \\ 56 & 1508 \\ 139 & 3638 \\ 136 & 3499 \\ 208 & 6374 \\ \hline & & d \\ 54 & 1336 \\ 133 & d \\ \hline & & d \\ 60 & 1315 \\ 134 & d \\ 140 & 1398 \\ \end{array}$

^{*a*} All data measured at ambient room temperature 23-26°. ^{*b*} Cm.² mole⁻¹ ohm⁻¹ in ~10⁻³ *M* nitromethane solutions. ^{*c*} Calculated from the Curie law, $\mu_{eff} = 2.84(\chi^{M}_{oot}T)^{1/2}$; all measurements refer to solids. ^{*d*} Accurate susceptibility not determined, diamagnetic. ^{*e*} Susceptibilities are slightly dependent on magnetic field strength.

The most obvious designations of the electronic configurations for the three series of complexes, as inferred from magnetic moments, would be d^0 , d^1 , d^2 for series I, II, and III, respectively. As the following

discussion will show, these d^n and corresponding formal oxidation state designations of the coordinated metal are not all easily rationalized with the electron spin resonance results. Such designations cannot be made with certainty on the basis of existing information.

TABLE II

POLAROGRAPHIC HALF-WAVE POTENTIALS IN ACETONITRILE

00001-011	
Couple	$E_{1/2}, v.^{a}$
$(V)^{-3} \rightleftharpoons (V)^{-2} + e^{-2}$	-0.49
$(Cr)^{-3} \rightleftharpoons (Cr)^{-2} + e^{-2}$	+0.16
$(W)^{-2} \rightleftharpoons (W)^{-} + e^{-}$	0.32
$(Mo)^{-2} \rightleftharpoons (Mo)^{-} + e^{-}$	0.36
$(V)^{-2} \rightleftharpoons (V)^{-} + e^{-}$	0.66
$(\mathbf{Cr})^{-2} \rightleftharpoons (\mathbf{Cr})^{-} + \mathbf{e}^{-}$	0.76
$(W)^- \rightleftharpoons (W)^0 + e^-$	0.88 ^b
$(M_0)^- \rightleftharpoons (M_0)^0 + e^-$	0.95^{b}
$(Cr)^{-} \rightleftharpoons (Cr)^{0} + e^{-}$	1.14^{b}
	Couple Couple $(V)^{-3} \rightleftharpoons (V)^{-2} + e^{-}$ $(Cr)^{-3} \rightleftharpoons (Cr)^{-2} + e^{-}$ $(W)^{-2} \rightleftharpoons (W)^{-} + e^{-}$ $(Mo)^{-2} \rightleftharpoons (Mo)^{-} + e^{-}$ $(V)^{-2} \rightleftharpoons (V)^{-} + e^{-}$ $(Cr)^{-2} \rightleftharpoons (Cr)^{-} + e^{-}$ $(Mo)^{-} \rightleftharpoons (Mo)^{0} + e^{-}$ $(Cr)^{-} \rightleftharpoons (Cr)^{0} + e^{-}$

^a Obtained using 0.05 M [(n-C₃H₇)₄N](ClO₄) as supporting electrolyte, and a platinum electrode; all results corrected for *iR* drop in polarographic cell. ^b Potentials become more negative and diffusion current decreases upon successive measurements in the same solution; these effects are probably caused by electrode filming.

The physical studies reported herein deal principally with the complexes of series II in which the metal is subjected to an octahedral ligand field with an unusually pronounced trigonal component. The synthetic studies demonstrate the interrelationship of complexes of the three series by simple oxidation-reduction reactions. Unlike the four-coordinate complexes already studied, ¹⁻⁴ such interrelationships of six-coordinate complexes by one-electron oxidation-reduction reactions have been effected previously, most notably with hexacyanide⁸ and tris(dipyridyl)⁹ species.

Synthetic Studies .- The starting point for the synthesis of all complexes of the $R = CF_3$ series is the reaction of bis(trifluoromethyl)-1,2-dithietene⁷ with the group VI hexacarbonyls to produce $[MS_6C_6(CF_3)_6]$ (M = Cr, Mo, W). Ethylcyclohexane has been found to be the most generally satisfactory solvent for these reactions. The use of a lower boiling solvent such as methylcyclohexane decreases the rate of reaction considerably, especially in the tungsten reaction, whereas the use of a higher boiling solvent results in increased decomposition, which is most pronounced in the chromium reaction. These reactions are somewhat analogous to the reactions of the thietene with $Ni(CO)_4$ and $Co_2(CO)_8$ to produce bis(thietene) complexes.⁴ As in these cases, the present reactions are viewed as, in effect, oxidation-reduction reactions in which the metal is oxidized to the IV or VI formal oxidation state (the latter is believed to be less likely as the following discussion demonstrates), and the ligand reduced to the thietene radical anion or dianion. These reactions tend to emphasize the strongly oxidizing pseudo-halogenoid character of the thietene in its reactions with carbonyls.¹⁰

⁽⁸⁾ For a recent review of cyanide complexes, see W. P. Griffith, Quart. Rev. (London), 16, 188 (1962).

⁽⁹⁾ S. Herzog, J. Inorg. Nucl. Chem., $\pmb{8},~557$ (1958), and subsequent publications.

⁽¹⁰⁾ Reactions of halogens and metal carbonyls result in oxidation of the metal with the formation of metal halides or carbonyl halides. A pertinent example here is the reaction of fluorine and $Mo(CO)_6$ at low temperature to yield MoF₈ [cf. R. D. Peacock, Proc. Chem. Soc., 59 (1957)].

TABLE III

ELECTRON SPIN RESONANCE RESULTS

,	Solution-				~100°K	
Complex	$\langle g \rangle$	$\langle A \rangle$, gauss	Solvent	8	8 T	A , gauss
$[CrS_6C_6(CF_3)_6]^-$	1.9941 ± 0.0003^{a}	$16.3 \pm 0.5 (Cr^{53}, I = 3/2)$	CHIOH	1.995 ± 0.002	1.995 ± 0.002	
$[MoS_6C_6(CF_3)_6]^-$	2.0097 ± 0.0003^{a}	$12.2 \pm 0.5 \text{ (Mo}_{95,97}, I = 5/2)$	CH3OH	2.011 ± 0.001	2.009 ± 0.001	$17.4 \pm 1.0 (A_{ })$
[WS.C.(CL.).]=	1 0010 + 0 00056		CILOH	1 097 1 0 000	1 002 0 002	$9.6 \pm 1.0 (A_{\perp})$
[W 56C6(CF3)6]	$1.9910 \pm 0.0005^{\circ}$	C .	CHIOH	1.987 ± 0.002	1.993 ± 0.002	
$[VS_6C_6(CN)_6]^{-2}$	$1.980 \pm 0.001^{\circ}$	$63.3 \pm 0.5^{\circ} (V^{1}, I = 7/2)$	CHCl ₈ -DMF	$1.974 \pm 0.005^{a,e}$	a,e	$100 \pm 2 (A_{ })$
						$45 \pm 1 (A_{\perp})$

^a Measured in dichloromethane. ^b Measured in CHCl₃-DMF (1:1 v./v.). ^c No observable splitting from W¹⁸³ (14.4%, I = 1/2). ^d See footnote 11. ^c $\Delta g = |0.005| \pm 0.002$; see footnote 11.

Reference to the polarographic half-wave potentials given in Table II shows that the neutral tris(thietene) complexes, like the related bis(thietene) Ni(IV), Co(IV), and Pt(IV) complexes, are very powerful oneelectron oxidizing agents. Comparison of these potentials with those for the bis complexes⁴ indicates that $[CrS_6C_6(CF_3)_6]$ is the most powerful oxidant of all such complexes thus far prepared. Treatment of $[MS_6C_6(CF_3)_6]$ with weakly basic solvents such as dry acetone and dry tetrahydrofuran causes reduction to $[MS_6C_6(CF_3)_6]^{-}$. This procedure is not recommended as a preparative method for the monoanions inasmuch as some reduction to the dianions also occurs. Treatment with more strongly basic solvents such as DMF causes complete reduction to the dianions, as does reaction with hydrazine, which is the recommended method of synthesis. As can be inferred from the potential data⁴ the dianions are stable to aerial oxidation in solution. One-electron reductions of these dianions could not be effected at potentials down to -1.5 v.

The monoanions are prepared in nearly quantitative yield by utilizing the strong oxidizing tendency of the neutral complexes as displayed by the following reactions carried out in dichloromethane solution with M = Cr, Mo, W.

 $[MS_{6}C_{6}(CF_{3})_{6}] + [MS_{6}C_{6}(CF_{3})_{6}]^{-2} \longrightarrow 2[MS_{6}C_{6}(CF_{3})_{6}]^{-1}$

Analytically pure salts can be directly isolated from the reaction mixture.

In the R = CN series only chromium and vanadium complexes were investigated. The species $[CrS_6C_6-(CN)_6]^{-3}$ is readily prepared and can be oxidized in high yield to the corresponding dianion by treatment with 1 equiv. of $[MoS_6C_6(CF_3)_6]$. Treatment of the chromium trianion with 2 equiv. of $[CrS_6C_6(CF_3)_6]$ gave an impure product which could not be definitely shown to contain $[CrS_6C_6(CN)_6]^-$, although the halfwave potentials indicate that this ion should be the thermodynamically favored product. Reaction of VCl₃ and Na₂S₂C₂(CN)₂ in the presence of air produced the oxidized product $[VS_6C_6(CN)_6]^{-2}$. It is clear from the half-wave potential data that the trianion, which is undoubtedly produced first, is readily oxidized by air.

The behavior of all tris complexes in solution with respect to oxidative and reductive stability as inferred from half-wave potentials is in good agreement with the generalizations relating to stabilities previously advanced on the basis of potentials for the bis complexes.⁴ Again, the potential data reflect (for the chromium complexes) the enhanced stabilization of the lower oxidation states in complexes containing the strongly electron-withdrawing cyano group compared to those with $R = CF_3$.

Electron Spin Resonance Results.—The molecular symmetry of the tris complexes is taken to be D_3 , in which case the one-electron t_{2g} -orbitals are split into $a_1 + e_a$. The e_g -orbitals are not further decomposed and are referred to as e_b . In complexes of this symmetry there is, strictly speaking, no distinction by symmetry of metal-ligand σ - and π -bonding. The metal-ligand π -bonds and the local π -orbitals of the chelate rings both span the representations $A_1 + A_2 +$ E which, of necessity, also include the metal nd_- , $(n + 1)s_-$, (n + 1)p-orbitals. The orbitals of interest are properly designated a_1^* , e_a^* , e_b^* inasmuch as they are antibonding orbitals of the general forms

$$\psi(\mathbf{a}_1^*) = C_{\mathbf{M}} [\alpha \mathbf{d}(\mathbf{a}_1) \pm \sqrt{1 - \alpha^2}(\mathbf{s})] - C_{\mathbf{L}}\sigma(\mathbf{a}_1) - C_{\mathbf{L}}'\pi(\mathbf{a}_1)$$
$$\psi(\mathbf{e}^*) = C_{\mathbf{M}} \mathbf{d}(\mathbf{e}) - C_{\mathbf{L}}\sigma(\mathbf{e}) - C_{\mathbf{L}}'\pi(\mathbf{e})$$

in which the σ - and π -orbitals are local molecular orbitals of the chelate rings with the indicated symmetries. We define the energy differences $e_a^* - a_1^*$ and $e_b^* - a_1^*$ as Δ_1 and Δ_2 , respectively. The $d(a_1)$ metal orbital is referred to as d_0 .

The results of the paramagnetic resonance measurements of the complexes $[MS_6C_6R_6]^-$ are given in terms of the parameters of the spin Hamiltonian

$$\mathfrak{K}_{s} = \beta_{e}[g_{||}S_{z}H_{z} + g_{\perp}(S_{x}H_{x} + S_{y}H_{y})] + A_{||}S_{z}I_{z} + A_{||}(S_{x}I_{x} + S_{y}I_{y}) \quad (1)$$

for measurements on rigid glass solutions, and in terms of

$$\mathfrak{K}_{\mathbf{s}} = \beta_{\mathbf{s}} \langle g \rangle \vec{S} \cdot \vec{H} + \langle A \rangle \vec{S} \cdot \vec{I}$$
(2)

for measurements made on fluid solutions. The motionally averaged parameters, $\langle g \rangle$ and $\langle A \rangle$, are given to a good approximation by

$$\langle g \rangle = \frac{1}{3}(g_{||} + 2g_{\perp}) \tag{3}$$

and

$$\langle A \rangle = \frac{1}{3}(A_{11} + 2A_{1})$$
 (4)

Implicit in the form of the spin Hamiltonian (eq. 1) is the assumption of an axially symmetric ligand field. The spin Hamiltonian parameters are given in Table III.¹¹ The *g*-values were corrected for second-order shifts due to hyperfine interaction where present.

The most striking feature of the paramagnetic resonance results is the lack of anisotropy of the *g*-tensor. For each complex $g_{\perp} \cong g_{\perp}$. We shall show that the magnetic resonance data cast severe doubt upon the most obvious electronic description of the series II complexes as nd^1 . This configuration, specifically d_0^1 , has been found in tris(acetylacetonato)titanium-(III),¹³ which is the only other example of a complex with trigonal symmetry having a doublet ground state.

1. g-Values.—The g-values for a d^1 configuration subjected to a trigonally distorted octahedral ligand field were first given by Bleaney.14 His equations are applicable only if $\Delta_2 >> \Delta_1$ and lead to g-values which differ significantly from 2 if $|\zeta|$, the one-electron spin-orbit coupling constant, and Δ_1 are of a comparable order of magnitude. Inasmuch as the observed g-values (cf. Table III) are all very near 2, it is expected that $|\zeta| << \Delta_1$, and that Δ_1 and Δ_2 are of comparable magnitude, but with $\Delta_1 < \Delta_2$. Under these conditions second-order perturbation theory can be applied to calculate g_{i1} and g_{\perp} . The observed g-values indicate that the trigonal distortion leaves a_1^* lower than e_a^* . It should be noted that if the e_a*-orbital were lowest, the g-values would deviate considerably from 2 and the complex would have a very short spin-lattice relaxation time. Under the above conditions the g-values are¹⁵

$$g_{\perp} = 2.00$$
 (5)

$$g_{\perp} = 2.00 - 2 \zeta | /\Delta_1 - 4 | \zeta' / \Delta_2 \qquad (6)$$

Recently McGarvey¹³ has obtained equations for $g_{||}$ and g_{\perp} which include the effects of covalency on the metal orbitals. For $\Delta_1 >> |\zeta|$ his equations reduce to the form of eq. 5 and 6 with the exception that $|\zeta|$ is replaced by $R_g[\zeta]$, where R_g is a reduction factor whose value depends on the extent of delocalization of the ground and excited state wave functions over the ligand system. Molecular orbital theory predicts $1 \geq R_g \geq 0.5$.

In Table IV those values of R_g are tabulated which would be required for consistency with the observed values or upper limits of $\Delta g = g_{\perp} - g_{\perp}$. Values of $|\zeta|$ were obtained from Dunn,¹⁶ and Δ_1 and Δ_2 were somewhat arbitrarily chosen as 10,000 and 20,000 cm.⁻¹,¹⁷ respectively. It is apparent that the g-

(11) In the vanadium complex, Δg was estimated from the relative widths of the solution hyperfine lines (Fig. 1) using Kivelson's expression¹² for the $M_{\rm I}$ dependence of the line width. In the expression

 $1/T_2 = \pi \sqrt{3}(a_1 + a_2 M_1 + a_3 M_1^2)$

the ratio a_2/a_3 is $-(7/2) \Delta g H_0/(A_{\parallel^1} - A_{\perp})$. Here $1/T_2$ is the peak-peak width of the Lorentzian derivative line associated with the nuclear quantum state M_1 , and H_0 is the magnetic field for resonance at the center of the hyperfine pattern. $A^{+} \parallel$ and A_{\perp} were determined from measurements in the glass and solution. The sign of Δg is not known since the signs of A_{\parallel} and A_{\perp} are not known.

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(17) These values are suggested from the optical spectra if the ground state configuration is taken as $(a_1^{\nu})^1$. The choice of Δ_1 and Δ_2 is not critical so long as $|\zeta| << \Delta_1$ and $\Delta_1 < \Delta_2$, which are the conditions necessary to explain the Δ_0 values if the configuration is $(a_1^{\nu})^1$.



Fig. 1.—E.s.r. spectrum of $[VS_6C_6(CN)_6]^{-2}$ in a 50:50 (v./v.) solution of CHCl₃ and DMF at room temperature.

values are in poor accord with theory if it is assumed that the metal configuration is $(a_1^*)^1$. The orbital reduction factors are in every case unrealistically small, and in one case R_g has the wrong sign.

TABLE IV

Orbital Reduction Factors Required for Consistency with g-Value Anisotropies^{α}

Complex	Δg	ζ, cm. ^{-1b}	$R_{\rm g}$
$[VS_6C_6(CN)_6]^{-2}$	0.005	250	0.05
$[CrS_6C_6(CF_3)_6]^-$	<0.002	380	<0.013
$[MoS_6C_6(CF_3)_6]^-$	0.002	1030	0.005
$[WS_6C_6(CF_3)_6]^-$	-0.006	$>2000^{\circ}$	(-) < 0.008

 $^a\,\mathrm{d}^1$ configuration assumed. b Values from ref. 16. c Assumed lower limit.

2. Anisotropic Hyperfine Interaction.—The anisotropic part of the hyperfine interaction tensor, with principal values $a_{,|} = A_{||} - \langle A \rangle$ and $a_{\perp} = A_{\perp} - \langle A \rangle$, was observed in $[VS_6C_6(CN)_6]^{-2}$ and $[MoS_6C_6(CF_3)_6]^{-}$. Ignoring small terms, McGarvey's eq. 11 and 12¹³ can be reduced to

$$a_{11} = 4P\langle 1/r^3 \rangle_{av}(R_a/7) \tag{7}$$

$$a_{\perp} = -2P\langle 1/r^3 \rangle_{\rm av}(R_{\rm a}/7) \tag{8}$$

in which $P = 2g_N\beta_e\beta_N$ and R_a is an orbital reduction factor having effectively the same theoretical limits as R_{g} ; g_{N} is the nuclear g-value and β_{N} the nuclear magneton. The value of $\langle 1/r^3 \rangle_{\rm av}$ was calculated from the SCF functions of Watson¹⁸ for V(IV) in the configuration 3p63d1, while this quantity was calculated for Mo(V) in the 4p⁶4d¹ configuration from the relationship given by Trees¹⁹ between $\langle 1/r^3 \rangle_{av}$ and ζ for the free ion. The values of $\langle 1/r^3 \rangle_{\rm av}$ so obtained are 2.50 \times 10²⁵ cm.⁻³ (V) and 3.4 \times 10²⁵ cm.⁻³ (Mo). The calculated values of $|a_{\perp}|$ are $107R_{\rm a}$ gauss for V⁵¹ and $36R_{\rm a}$ gauss for Mo⁹⁵ \sim Mo⁹⁷. Comparison with experimental values gives $R_a(V) = 0.34$ and $R_a(Mo) = 0.14$, both well below the theoretical lower limit for R_a assuming the $(a_1^*)^1$ configuration. It is to be noted that for a well established d¹ configuration in a trigonally distorted octahedral ligand field, McGarvey13 finds $|A_{\perp}| > |A_{\perp}|$ in contrast with these results where $|A_{\perp}| < A_{\perp}|$. These results cast serious doubt upon the identification of the ground state as $(a_1^*)^{\perp}$.

3. Isotropic Hyperfine Interactions.—In transition metal complexes isotropic hyperfine interaction can arise from two mechanisms: (a) direct admixture of the (n + 1)s wave function into the nd^m configuration,

⁽¹⁸⁾ R. E. Watson, Technical Report No. 12, Solid State and Molecular Theory Group, M.I.T., Cambridge, Mass., June 15, 1959.

⁽¹⁹⁾ R. E. Trees, Phys. Rev., 92, 308 (1953).

and (b) the admixture of excited states by configuration interaction leaving fractionally unpaired s-electrons. The latter mechanism was suggested by Abragam.²⁰ Both mechanisms are operative in D₃ symmetry since s- and d₀-orbitals both transform as A₁, thus allowing direct mixing of these orbitals. Values of $\langle A \rangle$ expected for the configurations np^{6} - $(n + 1)s^{1}$ have been calculated in order to obtain an estimate of an upper limit for the direct admixing of the s-function with a ground state d₀ wave function principally on the metal. The isotropic hyperfine interactions were estimated from an equation of Goudsmit,²¹ as modified by Trees,¹⁹ and using configuration energies tabulated by Moore.²²

Mechanisms (a) and (b) both contribute to $\langle A \rangle$ independently and it is difficult to assess individual contributions from each. For V⁵¹(d¹) the magnitude expected from (b) can be taken from VO⁺² hydrate which has $\langle A \rangle = 118$ gauss.²³ In this case (a) is ruled out on symmetry grounds.²⁴ Reference to Table V shows that (a) would become dominant in [VS₆-C₆(CN)₆]⁻² if the admixture of 4s-orbital were as large as 4–5%. The observed $\langle A \rangle = 63$ gauss would be inconsistent with anything more than about 3% admixture of 4s into the ground state.

TABLE V

Calculated Isotropic Hyperfine Interaction Constants $\langle A \rangle$ for the Configurations $np^{6}(n + 1)s^{a}$

Nucleus	n	$\langle A \rangle$, cm. ⁻¹	$\langle A angle$, gauss
V^{51}	3	0.39	4130
Cr ⁵³	3	-0.11	-1170
${ m Mo^{95}} \sim { m Mo^{97}}$	4	-0.20	-2120

^a All values obtained using g = 2.00.

4. Conclusions.—The paramagnetic resonance results are clearly inconsistent with an assumed d¹ metal ion configuration in a trigonal field. The principal discrepancies are summarized as follows: (a) $g_{\perp} \gtrsim g_{\parallel}$, rather than $g_{\perp} < g_{\parallel}$ for each complex; (b) $|A_{\parallel}| > |A_{\perp}|$ for $[VS_6C_6(CN)_6]^{-2}$ rather than the theoretically expected $|A_{\perp}| > |A_{\parallel}|$; (c) $g_{\parallel} \cong g_{\perp} > 2.0023$ for $[MOS_6C_6(CF_3)_6]^{-}$; and (d) $|a_{\parallel}|$, the anisotropic hyperfine splitting, is too small in $[VS_6C_6(CN)_6]^{-2}$ and $[MOS_6C_6(CF_3)_6]^{-}$.

In order to rationalize these results the assumption of D_3 symmetry is retained. It is then necessary to assume that the odd electron resides in a molecular orbital which is principally ligand in character. If this is the case, the g-values would be determined to a considerable extent by spin-orbit interactions with ligand atoms, mainly the sulfur atoms. It is known that sulfur-containing free radicals have g-values considerably greater than 2.0023. Some recent values are $g_1 = 2.003$, $g_2 = 2.035$, $g_3 = 2.055$.²⁵ It is possible that if the orbital of the odd electron were principally composed of ligand orbitals, g could exceed 2.0023, as is observed in $[MoS_6C_6(CF_3)_6]^-$. A similar explanation might also apply to the anomalously high g-value of $[Mo(CN)_8]^{-3}$.²⁶ In the general case the g-values would be determined by ligand and metal spin-orbit interactions, and the observed g-values would depend on the relative probability densities of the wave function on the ligands and metal. The small but observable values of $\langle A \rangle$ could arise from an exchange polarization of the metal s-electrons by the unpaired electron,²⁷ even if the latter were principally on the ligands. A mechanism resulting in a considerable metal anisotropic hyperfine interaction is difficult to justify on the basis of a ligand wave function for the odd electron, however.

We offer the suggestion that the complexes $[MS_6C_{6^-}]$ $(CF_3)_6$]⁻ and $[VS_6C_6(CN)_6]^{-2}$ might reasonably be considered to have a configuration d²l¹, rather than l²d¹, in which I represents a molecular orbital localized primarily on the ligands. This type of description would follow if the energy of the lowest principally metal antibonding orbital (a_1^*) were below the highest filled symmetry orbital of the ligand system while the orbitals e_a^* and e_b^* were above this orbital in energy. Extended Hückel-type calculations²⁸ on the isolated ligands $R_2C_2S_2^{-2}$ give the following energies (R = H) for the π -molecular orbitals designated in D₃ symmetry: -14.72 (a₂ + e), -13.47 (a₁ + e), -11.62 $(a_2^* + e^*)$, -6.47 e.v. $(a_1^* + e^*)$. It is assumed that the energy order is not affected by ligand-ligand interaction. We point out that the a_2^* ligand orbital cannot mix with the metal d-orbitals, but only with the (n +1)p_s-orbital, which is higher in energy. The a_2^* may then be essentially nonbonding and heavily ligand in character. The point at issue is whether a_1^* or a_2^* lies lower; our results are in agreement with the order $a_2^* > a_1^*$, at least for the series II complexes. If this order holds in the other series as well, electronic configurations consistent with the magnetic susceptibility and electron spin resonance results are as follows

z = 0	M = Cr, Mo, W	d^2 (S = 0)
z = -1	M = Cr, Mo, W	$d^{2}l^{1}$ $(S = 1/2)$
z = -2	M = V	$d^2 l^1 (S = 1/2)$
	M = Cr	$d^{3}l^{1}$ (S = 1)
	M = Mo, W	$d^{2}l^{2}$ (S = 0)

If correct, these configurations reflect the inability of the thietene ligand system to stabilize the high formal oxidation states V and VI. In Cr, Mo, and W compounds these valence states have been stabilized only when relatively electronegative and nonpolarizable donor atoms, such as oxygen, fluorine, and chlorine, are present in the coordination sphere. The thietene ligand system may be sufficiently polarizable such that it will, in effect, lose electrons to the coordinated metal rather than stabilize such high valence states. Indeed, previous infrared studies⁴ on bis-(thietene) complexes have revealed the tendency of the thietene ligand to lose electron density to the metal as the formal oxidation state of the metal is increased.

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Infrared Results.—Previous work⁴ on bis(thietene) complexes has shown that reasonable inferences concerning the qualitative extent of π -bonding between the ligand and the central metal can be drawn from the infrared spectra. The spectral feature of interest is the stretching frequency of the perturbed C==C portion of the chelated thietene rings. In salts these absorptions are readily distinguished from those of the tetraphenylarsonium ion, from which arise the only other bands above 1350 cm.⁻¹. The observed frequencies are given in Table VI; these are seen to be

Table VI

Perturbed C==C Stretching Frequencies in Thietene Complexes $^{\alpha}$

Complex ^b	Frequency, cm1
$[CrS_6C_6(CF_3)_6]$	1446
$[CrS_6C_6(CF_3)_6]^{-}$	1484
$[CrS_6C_6(CF_3)_6]^{-2}$	1511
$[MoS_6C_6(CF_3)_6]$	1455
$[MoS_6C_6(CF_3)_6]^-$	1508
$[MoS_6C_6(CF_3)_6]^{-2}$	1538
$[WS_6C_6(CF_3)_6]$	1474
$[WS_6C_6(CF_3)_6]^-$	1520
$[WS_6C_6(CF_3)_6]^{-2}$	1541
$(CF_3)_2C_2S_2(neat)$	1621

 $^{\alpha}$ Spectra of fluorolube mulls. b Measurements of salts refer to the tetraphenylarsonium salts.

substantially reduced from the free ligand value and to lie in the range 1440-1550 cm.⁻¹. The variation of the frequencies is the same as with the bis complexes,

viz., they increase for a given metal as the charge on the complex increases, *i.e.*, as the formal valence state of the metal decreases. The explanations of these variations in the bis and tris complexes are similar, and in the tris complexes are consistent with the electronic configurations proposed above. If in proceeding from the z = 0 to z = -2 complexes the a_2^* -orbital becomes occupied, the C==C frequencies should increase since this orbital has a node between the carbons and sulfurs and is bonding between the two carbons. That this simple explanation by itself is not completely satisfactory is seen from the observed frequency increase from $(Cr)^{-1}$ to $(Cr)^{-2}$. However, in the dianion the ea* orbital may be occupied, in which case bonding between ligand π -orbitals and the metal would be decreased.29

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(29) It could be reasonably argued that filling the a_i^* and e_a^* orbitals (with nonoccupancy of a_2^*) could cause the observed frequency trends since both of these orbitals are π -bonding with respect to local π -orbitals of the rings. Here we wish simply to point out that the infrared data are consistent with the proposed electronic configurations but are inconclusive in establishing them.

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A Nuclear Magnetic Resonance Study of Aqueous Pyruvate-Glycinate-Zinc(II) and Related Systems^{1a}

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Under the influence of bases (amines, cyanide, hydroxide) pyruvate (P^-) ions are shown to be dimerized and the dimer formation constant is evaluated. As has been observed with protons, Zn(II) ions also effect the hydration of pyruvate on association. The cause seems to lie in the cooperative operation of field and inductive effects, the former promoting the stability of ZnP^+_{diol} and the latter destablizing ZnP^+_{keto} . Pyruvate and glycinate ions in 1.0 *M* concentrations react incompletely to give a solution containing pyruvate dimer, the *cis* and *trans* forms of the ketimine, and one other major component, probably the carbinolamine. The rate of the *cis-trans* isomerization is acid catalyzed and the separate isomer peaks merge into one when glycine (GH) is added. The presence of Zn(II) or Ca(II) inhibits dimerization by complexing the reactants. The ligands in the "mixed" MPG complexes appear to be condensed as either the Schiff base or the carbinolamine. Over a period of 24 hr., transamination to give alanine is negligible. Alanate and glyoxalate ions react to give a Schiff base which is slow to tautomerize. The reaction is dramatically catalyzed by Zn(II).

The role that Schiff bases and their metal ion complexes play in transamination reactions has stimulated much interest in these compounds.²⁻⁷ While most attention has been focused on the highly significant

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pyridoxal systems, metal ions have been shown to catalyze a slow transamination between pyruvate and glycine⁸ and a faster reaction in the reverse direction between glyoxalate and alanine.⁹

At least one possible role of the metal ions in these last systems is to stabilize the Schiff bases by complexing since many Schiff bases, particularly those in the aliphatic series, are extensively dissociated in aqueous solutions. Indeed with pyruvate and glycinate mix-

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