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A Molecular Orbital Theory for Square Planar Metal Complexes

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The bonding in square planar metal complexes is described in terms of molecular orbitals. The relative single electron molecular orbital energies are estimated for the different types of π -electron systems. Both the d - d and charge transfer spectra of the halide and cyanide complexes of Ni^{2+} , Pd^{2+} , Pt^{2+} and Au^{3+} are discussed in terms of the derived molecular orbital scheme. The magnetic susceptibilities of diamagnetic d^8 -metal complexes are considered, and it is concluded that a substantial "ring current" exists in $K_2Ni(CN)_4 \cdot H_2O$.

Introduction

The metal ions which form square planar complexes with simple ligands have a d^8 -electronic configuration. The five degenerate d -orbitals of the uncomplexed metal ion split into four different levels in a square planar complex. Thus three orbital parameters are needed to describe the ligand field d -splittings.

Various efforts have been made to evaluate the d -orbital splittings in square planar metal complexes, and to assign the observed d - d spectral bands.²⁻⁸ The most complete calculation has been made for Pt^{2+} complexes by Fenske, Martin and Ruedenberg,⁶ and considerable confidence may be placed in their ordering of the d -orbitals. However, for other complexes the d -ordering may depend on the metal ion and the type of ligand under consideration.

It is the purpose of this paper to develop a molecular orbital theory for square planar metal complexes. Both the spectral and magnetic properties of typical square planar complexes of Ni^{2+} , Pd^{2+} , Pt^{2+} and Au^{3+} will be considered in order to arrive at consistent values for the molecular orbital energies. However, in contrast to previous workers, effort will be concentrated on the assignments of the charge transfer bands of representative square planar complexes.

Molecular Orbitals for Square Planar Complexes.—

Figure 1 shows a square planar complex in a coordinate system with the central atom at the origin, and the four ligands along the x - and y -axes. The orbital transformation scheme in the D_{4h} symmetry is given in Table I.

TABLE I

ORBITAL TRANSFORMATION SCHEME IN D_{4h} SYMMETRY

Representation	Metal orbitals	Ligand orbitals
a_{1g}	d_{z^2}, s	$1/2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)$
a_{2g}	..	$1/2(\pi_{1h} + \pi_{2h} + \pi_{3h} + \pi_{4h})$
a_{2u}	p_z	$1/2(\pi_{1v} + \pi_{2v} + \pi_{3v} + \pi_{4v})$
b_{1g}	$d_{x^2 - y^2}$	$1/2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)$
b_{2g}	d_{xy}	$1/2(\pi_{1h} - \pi_{2h} + \pi_{3h} - \pi_{4h})$
b_{2u}	..	$1/2(\pi_{1v} - \pi_{2v} + \pi_{3v} - \pi_{4v})$
e_g	d_{yz}, d_{zx}	$1/\sqrt{2}(\pi_{2v} - \pi_{4v}), 1/\sqrt{2}(\pi_{1v} - \pi_{3v})$
e_u	p_x, p_y	$1/\sqrt{2}(\sigma_1 - \sigma_3), 1/\sqrt{2}(\sigma_2 - \sigma_4)$ $1/\sqrt{2}(\pi_{2h} - \pi_{4h}), 1/\sqrt{2}(\pi_{1h} - \pi_{3h})$

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The single electron molecular orbitals are approximated as

$$\Psi(\text{m.o.}) = C_{M(i)}\Phi(\text{metal}) + C_{L(j)}\Phi(\text{ligand}) \quad (1)$$

where the C 's are subject to the usual normalization and orthogonality restrictions. The pure σ -orbitals are

$$\Psi[a_{1g}(\sigma)] = C_{M(1)}\Phi[nd_{z^2}] + C_{M(2)}\Phi[(n+1)s] + C_L\Phi[1/2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)] \quad (2)$$

$$\Psi[b_{1g}(\sigma)] = C_M\Phi[nd_{x^2 - y^2}] + C_L\Phi[1/2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)] \quad (3)$$

The form of the π -orbitals depends on the type of ligand under consideration. Square planar complexes in which the ligands themselves have no π -orbital system (Cl^- , Br^- , H_2O , NH_3) will be case 1; complexes in which the ligands have a π -system (CN^-), and thus both π -bonding (π^b) and π -antibonding (π^*) ligand orbitals must be considered, will be case 2.

Case 1.—The pure π -orbitals are

$$\Psi[a_{2g}(\pi)] = \Phi[1/2(\pi_{1h} + \pi_{2h} + \pi_{3h} + \pi_{4h})] \quad (4)$$

$$\Psi[a_{2u}(\pi)] = C_M\Phi[(n+1)p_z] + C_L\Phi[1/2(\pi_{1v} + \pi_{2v} + \pi_{3v} + \pi_{4v})] \quad (5)$$

$$\Psi[b_{2g}(\pi)] = C_M\Phi[nd_{xy}] + C_L\Phi[1/2(\pi_{1h} - \pi_{2h} + \pi_{3h} - \pi_{4h})] \quad (6)$$

$$\Psi[b_{2u}(\pi)] = \Phi[1/2(\pi_{1v} - \pi_{2v} + \pi_{3v} - \pi_{4v})] \quad (7)$$

$$\Psi_1[e_g(\pi)] = C_M\Phi[nd_{xz}] + C_L\Phi\left[\frac{1}{\sqrt{2}}(\pi_{1v} - \pi_{3v})\right] \quad (8)$$

$$\Psi_{11}[e_g(\pi)] = C_M\Phi[nd_{yz}] + C_L\Phi\left[\frac{1}{\sqrt{2}}(\pi_{2v} - \pi_{4v})\right] \quad (9)$$

The mixed σ - and π -orbitals are

$$\Psi_1[e_u(\sigma, \pi)] = C_M\Phi[(n+1)p_z] + C_{L(1)}\Phi\left[\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3)\right] + C_{L(2)}\Phi\left[\frac{1}{\sqrt{2}}(\pi_{2h} - \pi_{4h})\right] \quad (10)$$

$$\Psi_{11}[e_u(\sigma, \pi)] = C_M\Phi[(n+1)p_y] + C_{L(1)}\Phi\left[\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)\right] + C_{L(3)}\Phi\left[\frac{1}{\sqrt{2}}(\pi_{1h} - \pi_{3h})\right] \quad (11)$$

Case 2.—The pure π -orbitals are

$$\Psi[a_{2g}(\pi^b)] = \Phi[1/2(\pi_{1h}^b + \pi_{2h}^b + \pi_{3h}^b + \pi_{4h}^b)] \quad (12)$$

$$\Psi[a_{2g}(\pi^*)] = \Phi[1/2(\pi_{1h}^* + \pi_{2h}^* + \pi_{3h}^* + \pi_{4h}^*)] \quad (13)$$

$$\Psi[a_{2u}(\pi)] = C_M\Phi[(n+1)p_z] + C_{L(1)}\Phi[1/2(\pi_{1v}^b + \pi_{1v}^* + \pi_{3v}^b + \pi_{3v}^*)] + C_{L(2)}\Phi[1/2(\pi_{2v}^* + \pi_{2v}^* + \pi_{3v}^* + \pi_{4v}^*)] \quad (14)$$

$$\Psi[b_{2g}(\pi)] = C_M\Phi[nd_{xy}] + C_{L(1)}\Phi[1/2(\pi_{1h}^b - \pi_{2h}^b + \pi_{3h}^b - \pi_{4h}^b)] + C_{L(2)}\Phi[1/2(\pi_{1h}^* - \pi_{2h}^* + \pi_{3h}^* - \pi_{4h}^*)] \quad (15)$$

$$\Psi[b_{2u}(\pi^b)] = \Phi[1/2(\pi_{1v}^b - \pi_{2v}^b + \pi_{3v}^b - \pi_{4v}^b)] \quad (16)$$

$$\Psi[b_{2u}(\pi^*)] = \Phi[1/2(\pi_{1v}^* - \pi_{2v}^* + \pi_{3v}^* - \pi_{4v}^*)] \quad (17)$$

$$\Psi_1[e_g(\pi)] = C_M\Phi[nd_{xz}] + C_{L(1)}\Phi\left[\frac{1}{\sqrt{2}}(\pi_{1v}^b - \pi_{3v}^b)\right] + C_{L(2)}\Phi\left[\frac{1}{\sqrt{2}}(\pi_{1v}^* - \pi_{3v}^*)\right] \quad (18)$$

$$\Psi_{11}[e_g(\pi)] = C_M\Phi[nd_{yz}] + C_{L(1)}\Phi\left[\frac{1}{\sqrt{2}}(\pi_{2v}^b - \pi_{4v}^b)\right] + C_{L(2)}\Phi\left[\frac{1}{\sqrt{2}}(\pi_{2v}^* - \pi_{4v}^*)\right] \quad (19)$$

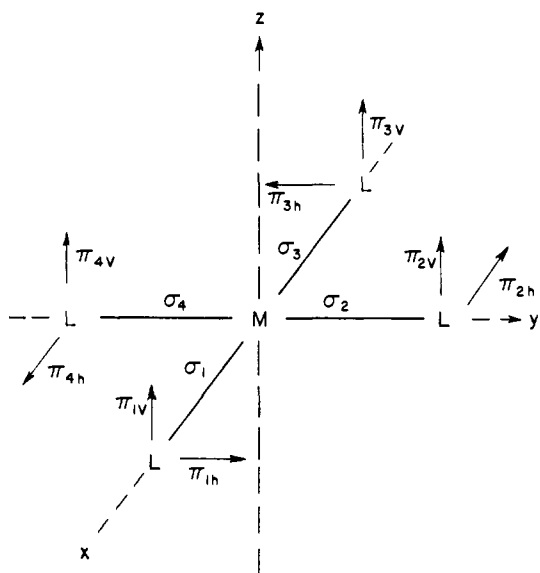


Fig. 1.—A molecular orbital coordinate system for a square planar metal complex.

The mixed σ - and π -orbitals are

$$\Psi_{I1}[e_u(\sigma, \pi)] = C_M \Phi[(n+1)p_x] + C_{L(1)} \Phi \left[\frac{1}{\sqrt{2}} (\sigma_1 - \sigma_3) \right] + C_{L(2)} \Phi \left[\frac{1}{\sqrt{2}} (\pi_{2h}^b - \pi_{4h}^b) \right] + C_{L(3)} \Phi \left[\frac{1}{\sqrt{2}} (\pi_{2h}^* - \pi_{4h}^*) \right] \quad (20)$$

$$\Psi_{I1}[e_u(\sigma, \pi)] = C_M \Phi[(n+1)p_y] + C_{L(1)} \Phi \left[\frac{1}{\sqrt{2}} (\sigma_2 - \sigma_4) \right] + C_{L(2)} \Phi \left[\frac{1}{\sqrt{2}} (\pi_{1h}^b - \pi_{3h}^b) \right] + C_{L(3)} \Phi \left[\frac{1}{\sqrt{2}} (\pi_{1h}^* - \pi_{3h}^*) \right] \quad (21)$$

The following general rules were adhered to in estimating the relative energies of the single electron molecular orbitals: (1) The order of the coulomb energies is taken to be σ (ligand), π^b (ligand), nd (metal), $(n+1)s$ (metal), π^* (ligand), $(n+1)p$ (metal). (2) The amount of mixing of atomic orbitals in the molecular orbitals is roughly proportional to atomic orbital overlap and inversely proportional to their coulomb energy difference. (3) Other things being approximately equal, σ -bonding molecular orbitals are more stable than π -bonding molecular orbitals, and σ -antibonding molecular orbitals correspondingly less stable than π -antibonding molecular orbitals. (4) Interactions among the ligands themselves are expressed in terms of a ligand-ligand exchange integral β : the sign of this interaction for each molecular orbital is another factor in the final relative ordering. (5) The relative molecular orbital ordering is considered final only if it is fully consistent with the available experimental results: exact differences in the single electron molecular orbital levels can only be obtained from experiment.

The general molecular orbital energy level schemes arrived at for square planar complexes are given in Fig. 2 (case 1) and Fig. 3 (case 2). Group molecular orbital overlap integrals (for $\text{Ni}(\text{CN})_4^{2-}$) and ligand exchange interactions are summarized in Table II.

Almost all square planar complexes with simple ligands are diamagnetic and contain a metal ion with the d^8 -electronic configuration. Thus the ground state is $^1A_{1g}$. The lowest energy excited states will be described separately for case 1 and case 2.

Case 1.—There are three spin-allowed $d-d$ type transitions, corresponding to the one electron transitions $b_{2g}(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ($^1A_{1g} \rightarrow ^1A_{2g}$), $a_{1g}(\sigma^*) \rightarrow b_{1g}(\sigma^*)$

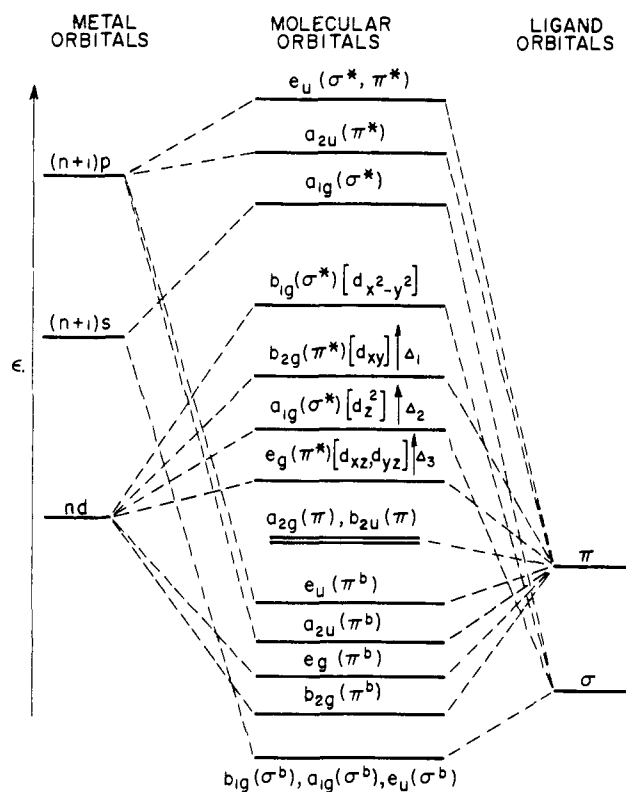


Fig. 2.—Molecular orbital energy level scheme for square planar metal complexes in which there is no intra-ligand π -orbital system (case 1).

($^1A_{1g} \rightarrow ^1B_{1g}$) and $e_g(\pi^*) \rightarrow b_{1g}(\sigma^*)$ ($^1A_{1g} \rightarrow ^1E_g$). All these are parity forbidden as electric dipole transitions. Two allowed charge transfer transitions may be anticipated, corresponding to the one-electron transitions $b_{2u}(\pi) \rightarrow b_{1g}(\sigma^*)$ ($^1A_{1g} \rightarrow ^1A_{2u}$) and $e_u(\pi^b) \rightarrow b_{1g}(\sigma^*)$

TABLE II
GROUP OVERLAP INTEGRALS AND LIGAND-LIGAND INTERACTIONS FOR SQUARE PLANAR METAL COMPLEXES

Molecular orbital	Metal orbital	Ligand orbitals	G_{ij}^a	Ligand-ligand interaction
$\Psi[a_{1g}(\sigma)]$	$[nd_{z^2}]$ $[(n+1)s]$	$[1/2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)]$ $[1/2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4)]$	0.161 .895
$\Psi[b_{1g}(\sigma)]$	$[nd_{x^2-y^2}]$	$[1/2(\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4)]$.279
$\Psi[a_{2g}(\pi)]$	$[1/2(\pi_{1h} + \pi_{2h} + \pi_{3h} + \pi_{4h})]$...	$-2\beta(h,h)$
$\Psi[a_{2u}(\pi)]$	$[(n+1)p_z]$	$[1/2(\pi_{1v} + \pi_{2v} + \pi_{3v} + \pi_{4v})]$	0.464	$+2\beta(v,v)$
$\Psi[b_{2g}(\pi)]$	$[nd_{xy}]$	$[1/2(\pi_{1h} - \pi_{2h} + \pi_{3h} - \pi_{4h})]$	0.166	$+2\beta(h,h)$
$\Psi[b_{2u}(\pi)]$	$[1/2(\pi_{1v} - \pi_{2v} + \pi_{3v} - \pi_{4v})]$...	$-2\beta(v,v)$
$\Psi_1[e_g(\pi)]$	$[nd_{xz}]$	$[\frac{1}{\sqrt{2}}(\pi_{1v} - \pi_{3v})]$	0.117
$\Psi_{II}[e_g(\pi)]$	$[nd_{yz}]$	$[\frac{1}{\sqrt{2}}(\pi_{2v} - \pi_{4v})]$.117
$\Psi_1[e_u(\sigma, \pi)]$	$[(n+1)p_x]$	$[\frac{1}{\sqrt{2}}(\sigma_1 - \sigma_3)]$.769
	$[(n+1)p_z]$	$[\frac{1}{\sqrt{2}}(\pi_{2h} - \pi_{4h})]$.328
$\Psi_{II}[e_u(\sigma, \pi)]$	$[(n+1)p_y]$	$[\frac{1}{\sqrt{2}}(\sigma_2 - \sigma_4)]$.769
	$[(n+1)p_y]$	$[\frac{1}{\sqrt{2}}(\pi_{1h} - \pi_{3h})]$.328

^a The group overlap integrals are for $\text{Ni}(\text{CN})_4^{2-}$. The atomic wave functions are: 3d and 4s radial functions for nickel from ref. 16; 2s carbon radial function from ref. 17; 2p carbon radial function from ref. 18; the 4p nickel radial function is estimated as $\Phi(4p) = R_{sp}(1.40)$, where $R_{sp}(1.40)$ is a Slater orbital with exponent 1.40. The Ni-C distance is taken to be 1.90 Å, averaged from the data given in ref. 21.

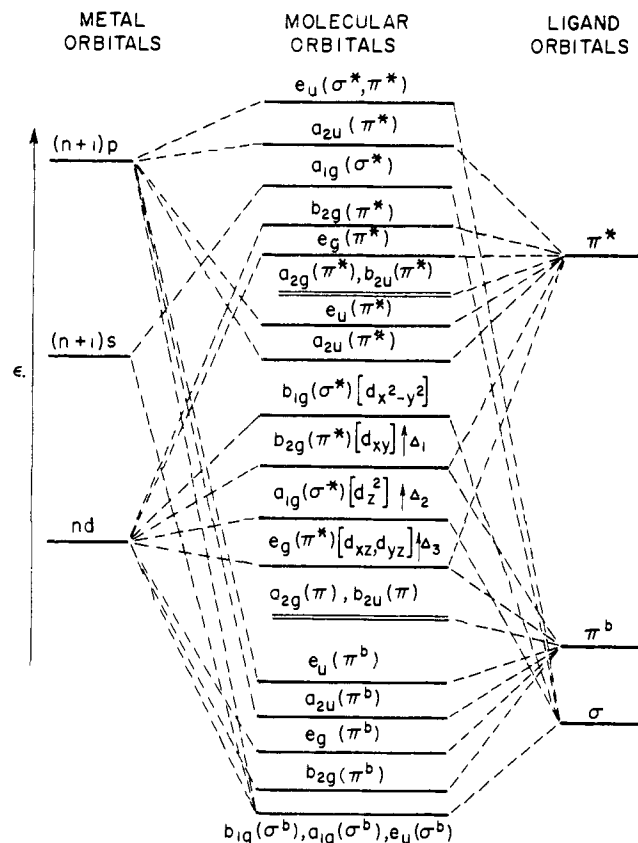


Fig. 3.—Molecular orbital energy level scheme for square planar metal complexes in which the ligands themselves have a π -orbital system (case 2).

(${}^1A_{1g} \rightarrow {}^1E_u$). These are transitions from molecular orbitals essentially localized on the ligands to molecular orbitals essentially localized on the metal atom. An examination of the transition moment integrals for these two transitions reveals that, for any reasonable molecular orbitals, the ${}^1A_{1g} \rightarrow {}^1E_u$ transition will be more intense than ${}^1A_{1g} \rightarrow {}^1A_{2u}$.

Case 2.—There are three $d-d$ transitions; ${}^1A_{1g} \rightarrow {}^1A_{2g}$, ${}^1A_{1g} \rightarrow {}^1B_{1g}$ and ${}^1A_{1g} \rightarrow {}^1E_g$, as in case 1. The charge transfer bands of lowest energy are expected to involve transitions from the highest filled metal orbitals to the most stable empty "ligand" molecular orbital, the $a_{2u}(\pi^*)$. The first charge transfer transition is $b_{2g}(\pi^*) \rightarrow a_{2u}(\pi^*)$ (${}^1A_{1g} \rightarrow {}^1B_{1u}$). This transition is orbitally forbidden and should have relatively little intensity. The second charge transfer band corresponds to the transition $a_{1g}(\sigma^*) \rightarrow a_{2u}(\pi^*)$ (${}^1A_{1g} \rightarrow {}^1A_{2u}$). The energy of this transition is calculated to be $\Delta E({}^1A_{1g} \rightarrow {}^1B_{1u}) + \Delta_2$, corrected for differences in interelectronic-repulsion energies in the ${}^1A_{2u}$ and ${}^1B_{1u}$ excited states. The third charge transfer transition is $e_g(\pi^*) \rightarrow a_{2u}(\pi^*)$ (${}^1A_{1g} \rightarrow {}^1E_u$), and is calculated to be $\Delta E({}^1A_{1g} \rightarrow {}^1B_{1u}) + \Delta_2 + \Delta_3$, again corrected for repulsion differences in the 1E_u and ${}^1B_{1u}$ excited states. A summary of the calculated orbital and interelectronic-repulsion energies of all the excited states of interest for case 2 is given in Table III.

The ${}^1A_{1g} \rightarrow {}^1A_{2u}$ and ${}^1A_{1g} \rightarrow {}^1E_u$ transitions are allowed, with the ${}^1A_{1g} \rightarrow {}^1E_u$ transition expected to have considerably greater intensity. Thus a three-band charge transfer spectrum, with an intensity order ${}^1A_{1g} \rightarrow {}^1E_u > {}^1A_{1g} \rightarrow {}^1A_{2u} > {}^1A_{1g} \rightarrow {}^1B_{1u}$, should be typical of square planar complexes with case 2 type ligands.

Spectral Properties of Square Planar Metal Complexes. A. Halide Complexes (Case 1).—The com-

TABLE III
ORBITAL AND INTERELECTRONIC-REPULSION ENERGIES OF SOME EXCITED STATES OF INTEREST FOR AN nd^8 SQUARE PLANAR COMPLEX

Term designation	Orbital energy ^a	Slater-Condon energy ^{a,b}
A. Singlet terms	${}^1A_{1g}$ (ground state)	...
	${}^1A_{2g}$ Δ_1	$-35F_4$
$d-d$ transitions	${}^1B_{1g}$ $\Delta_1 + \Delta_2$	$-4F_2 - 15F_4$
	1E_g $\Delta_1 + \Delta_2 + \Delta_3$	$-3F_2 - 20F_4$
Charge transfer transitions	${}^1B_{1u}$... $\Delta E({}^1B_{1u})$...
	${}^1A_{2u}$ $\Delta E({}^1B_{1u}) + \Delta_2$	$-20F_2 + 100F_4$
	1E_u $\Delta E({}^1B_{1u}) + \Delta_2 + \Delta_3$	$-15F_2 + 75F_4$
B. Triplet terms	${}^3A_{1g}$ Δ_1	$-105F_4$
$d-d$ transitions	${}^3B_{1g}$ $\Delta_1 + \Delta_2$	$-12F_2 - 45F_4$
	3E_g $\Delta_1 + \Delta_2 + \Delta_3$	$-9F_2 - 60F_4$

^a Referred to the ground state as zero. ^b For the approximations used to estimate the Slater-Condon energy for the charge transfer transitions, see ref. 19.

plexes PdX_4^{2-} , PtX_4^{2-} and AuX_4^- ($X^- = \text{halide}$) are square planar and diamagnetic. The spectra of solid samples of K_2PdCl_4 and K_2PdBr_4 have been measured by Harris, Livingstone and Reece,⁹ and by Yamada.¹² Three bands are observed which may be assigned to $d-d$ transitions. In solution, $PdCl_4^{2-}$ and $PdBr_4^{2-}$ show two charge transfer bands.

The interpretation of the spectrum of $PtCl_4^{2-}$ is complicated by the presence of one or more "spin-forbidden" bands. However, $PtCl_4^{2-}$ seems to exhibit the three spin-allowed $d-d$ bands, and one charge transfer band. The spectra of the $AuCl_4^-$ and $AuBr_4^-$ complexes clearly show the two charge transfer bands.¹⁰

Assignments of the spectra of these halide complexes, in terms of the derived molecular orbital level scheme for case 1, are given in Table IV. The values of the single electron parameters Δ_1 , Δ_2 and Δ_3 also are calculated and are given in Table V for comparison purposes.

B. Cyanide Complexes (Case 2).—The spectra of the square planar $Ni(CN)_4^{2-}$, $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$ complexes are given in Table IV. Each complex exhibits the expected three charge transfer bands, but the $d-d$ bands for the most part are obscured by these charge transfer bands. For $Ni(CN)_4^{2-}$, there are two shoulders on the tail of the first charge transfer band. These shoulders probably represent at least two $d-d$ transitions. The charge transfer spectrum of $Au(CN)_4^-$ appears at higher energies than for $Pt(CN)_4^{2-}$. Thus only one of the expected three charge transfer bands is seen below $50,000 \text{ cm}^{-1}$. The significance of this is discussed later.

Assignments of the spectra and the calculated values of Δ_1 , Δ_2 and Δ_3 for the cyanide complexes are given in Tables IV and V, respectively.

Magnetic Properties of Square Planar Metal Complexes.—The magnetic susceptibility of the diamagnetic d^8 square planar metal complexes is given by

$$X = \frac{1}{3}(2X_{\perp} + X_{\parallel}) \quad (22)$$

where

$$X_{\perp} = X_A + X_{H.F.(\perp)} \quad (23)$$

$$X_{\parallel} = X_A + X_{H.F.(\parallel)} + X_{ring} \quad (24)$$

In eq. 23 and 24, X_A is the atomic contribution for the molecule in question (the sum of the Pascal constants), X_{ring} represents the expected diamagnetic contribution of the metal-ligand π -molecular orbital system (analogous to the ring diamagnetism in benzene) and

$$X_{H.F.(\perp)} = \frac{-2}{g_m} N\beta^2 \frac{|\langle \psi_0 | L_x + 2S_x | \psi_1 \rangle|^2}{\Delta E_{0,1}} \quad (25)$$

$$X_{H.F.(\parallel)} = \frac{-2}{g_m} N\beta^2 \frac{|\langle \psi_0 | L_z + 2S_z | \psi_1 \rangle|^2}{\Delta E_{0,1}} \quad (26)$$

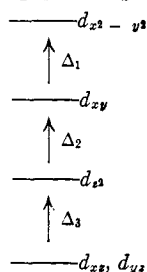
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TABLE IV
 SPECTRAL PROPERTIES OF SQUARE PLANAR METAL COMPLEXES

Complex (sample)	ν_{\max} , cm. ⁻¹	ϵ_{\max}	Assignment	Reference to exptl. work
Case 1				
PdCl ₄ ²⁻ (solid K ₂ PdCl ₄)	16,700	¹ A _{1g} → ¹ A _{2g}	9, 12, 20
	21,500	¹ A _{1g} → ¹ B _{1g}	
	23,300	¹ A _{1g} → ¹ E _{1g}	
	36,000	12,000	¹ A _{1g} → ¹ A _{2u}	
(aq. soln., excess Cl ⁻)	44,900	30,000	¹ A _{1g} → ¹ E _u	9
	16,000	¹ A _{1g} → ¹ A _{2g}	
	20,000	¹ A _{1g} → ¹ B _{1g}	
	26,000 ^a	¹ A _{1g} → ¹ E _g	
(aq. soln., excess Br ⁻)	30,100	10,400	¹ A _{1g} → ¹ A _{2u}	2a
	40,500	30,400	¹ A _{1g} → ¹ E _u	
	17,700	2.6	¹ A _{1g} → ³ A _{2g}	
	21,000	15	¹ A _{1g} → ¹ A _{2g}	
PtCl ₄ ²⁻ (aq. soln.)	25,500	59	¹ A _{1g} → ¹ B _{1g}	2a
	30,200	64	¹ A _{1g} → ¹ E _g	
	(37,900)	250	b	
	46,000	9,580	¹ A _{1g} → ¹ A _{2u}	
PtBr ₄ ²⁻ (aq. soln., 1 MBr ⁻)	16,700	5	¹ A _{1g} → ³ A _{2g}	This work
	19,700	15	¹ A _{1g} → ¹ A _{2g}	
	24,300	100	¹ A _{1g} → ¹ B _{1g}	
	28,200	120	¹ A _{1g} → ¹ E _g	
AuCl ₄ ⁻ (aq. soln.)	37,300	7000	¹ A _{1g} → ¹ A _{2u}	10
	31,800	4,570	¹ A _{1g} → ¹ A _{2u}	
	44,200	29,500	¹ A _{1g} → ¹ E _u	
	26,300	5,010	¹ A _{1g} → ¹ A _{2u}	
AuBr ₄ ⁻ (aq. soln.)	39,400	38,900	¹ A _{1g} → ¹ E _u	10
Case 2				
Ni(CN) ₄ ²⁻ (aq. soln.)	(22,500)	2	¹ A _{1g} → ¹ A _{2g}	This work
	(30,500)	250	¹ A _{1g} → ¹ B _{1g}	
	32,300	700	¹ A _{1g} → ¹ B _{1u}	
	35,200	4,200	¹ A _{1g} → ¹ A _{2u}	
Pd(CN) ₄ ²⁻ (aq. soln.)	37,600	10,600	¹ A _{1g} → ¹ E _u	20
	41,600	1,200	¹ A _{1g} → ¹ B _{1u}	
	45,400	7,200	¹ A _{1g} → ¹ A _{2u}	
	47,200	9,000	¹ A _{1g} → ¹ E _u	
Pt(CN) ₄ ²⁻ (aq. soln.)	35,720	1,590	¹ A _{1g} → ¹ B _{1u}	22
	(38,680)	26,000	¹ A _{1g} → ¹ E _u	
	39,180	29,500	¹ A _{1g} → ¹ E _u	
	41,320	1,850	¹ A _{1g} → ¹ A _{2u}	
Au(CN) ₄ ⁻ (aq. soln.)	30,960	51	¹ A _{1g} → ¹ A _{2g}	22
	37,880	331	¹ A _{1g} → ¹ B _{1g}	
	46,080	2,400	¹ A _{1g} → ¹ B _{1u}	

^a This band is found at 21,700 cm.⁻¹ in the K₂PdBr₄·2H₂O crystal; see ref. 12. ^b Possibly a "spin-forbidden" charge transfer transition.

 TABLE V
 METAL *d*-ORBITAL ENERGIES FOR SELECTED SQUARE PLANAR COMPLEXES


Orbital energy differences (cm.⁻¹) for $F_2 = 10F_4 = 700$ cm.⁻¹

Complex ion	Δ_1	Δ_2	Δ_3
PdCl ₄ ²⁻	19,150	6,200	1450
PdBr ₄ ²⁻	18,450	5,400	5650 (1350) ^a
PtCl ₄ ²⁻	23,450	5,900	4350
PtBr ₄ ²⁻	22,150	6,000	3550
AuCl ₄ ⁻	>20,000
AuBr ₄ ⁻	>20,000
Ni(CN) ₄ ²⁻	24,950	9,900	650
Pd(CN) ₄ ²⁻	>30,000	10,800	50
Pt(CN) ₄ ²⁻	>30,000	12,600	-4140
Au(CN) ₄ ⁻	33,410	10,620

^a The value of Δ_3 for K₂PdBr₄·2H₂O.

where g_m is the degeneracy of the ground state and $\Delta E_{0,i}$ is the energy separation between the ground state

ψ_0 and excited state ψ_i . For the d^8 complexes under consideration, the ground state is ¹A_{1g}, and eq. 25 and 26 reduce to

$$X_{H.F.(L)} = \frac{(C_M)^2 4N\beta^2}{\Delta E(^1A_{1g} \rightarrow ^1E_g)} \quad (27)$$

$$X_{H.F.(||)} = \frac{(C_M)^2 16N\beta^2}{\Delta E(^1A_{1g} \rightarrow ^1A_{2g})} \quad (28)$$

The magnetic susceptibility of a single crystal of K₂Ni(CN)₄·H₂O has been measured by Rogers.¹¹ The values he obtained were

$$X_{||} = -127.8 \times 10^{-6} \text{ (c.g.s.)}$$

$$X_{\perp} = -146 \times 10^{-6} \text{ (c.g.s.)}$$

Subtracting eq. 24 and eq. 23, the unknown X_A is eliminated, yielding

$$X_{\perp} - X_{||} - (X_{H.F.(L)} - X_{H.F.(||)}) = -X_{ring} \quad (29)$$

Using the experimental values for the ΔE 's, $X_{H.F.(L)} = 26 \times 10^{-6}$ and $X_{H.F.(||)} = 142 \times 10^{-6}$ are calculated; this gives $X_{ring} = -98 \times 10^{-6}$.

Discussion

The metal orbitals involved in σ -bonding in square planar complexes are the nd_{z^2} , $nd_{x^2-y^2}$, $(n+1)s$, $(n+1)p_x$ and $(n+1)p_y$. The $nd_{x^2-y^2}$, $(n+1)s$, $(n+1)p_x$ and $(n+1)p_y$ orbitals account for most of the σ -bonding, judging from the values of the overlap integrals in Table II, and the nd_{z^2} makes only a minor contribution. The most important π -molecular orbital is the a_{2u} , consisting of the $(n+1)p_z$ metal orbital and a combination of the four ligand π_v -orbitals. This gives a very stable π -bonding orbital (with only a single node in the molecular plane) which may be called the "ring" π -orbital. All the other pure π -molecular orbitals have an equal number of electrons in their bonding and antibonding levels.

The tendency of nd^8 -metal ions to form square planar complexes increases in the order Ni²⁺ < Pd²⁺ < Pt²⁺. Two features of the molecular orbital bonding scheme are consistent with this observation. First, the availability of the $nd_{x^2-y^2}$ metal orbital for σ -bonding undoubtedly increases in going from Ni²⁺ to Pt²⁺ (NiCl₄²⁻ is tetrahedral; PdCl₄²⁻ and PtCl₄²⁻ are square planar). Second, the square planar configuration is stabilized by the ring π -bonding, which is expected to increase from Ni²⁺ to Pt²⁺. The addition of a fifth group above the square plane drastically decreases the ring π -bonding, by tying up the $(n+1)p_z$ orbital in σ -bonding.

The assignments of the electronic spectra of the square planar halide and cyanide complexes of Ni²⁺, Pd²⁺, Pt²⁺ and Au³⁺ are given in Table IV. The halide complexes will be considered first. The spectra of K₂PdCl₄ and K₂PdBr₄ show three bands which may be assigned to d - d transitions. In the molecular orbital energy level scheme for case 1 ligands, the order of the single electron molecular orbitals is reasonably expected to be $e_g(\pi^*)$, $a_{1g}(\sigma^*)$, $b_{2g}(\pi^*)$ and $b_{1g}(\sigma^*)$. Thus the bands are assigned ¹A_{1g} → ¹A_{2g}, ¹A_{1g} → ¹B_{1g} and ¹A_{1g} → ¹E_g in order of increasing energy. The energy order of the single electron molecular orbitals deduced here is consistent with the results of a "complete" electrostatic calculation of square planar Pt²⁺ complexes performed by Fenske, *et al.*⁸

The spectra of PtCl₄²⁻ and PtBr₄²⁻ are slightly more complicated; the first band is quite weak and is assigned as the first spin-forbidden transition, ¹A_{1g} → ³A_{2g}. The spin-allowed transitions are assigned in the same way as for the PdX₄²⁻ complexes. The spectra of single crystals of K₂PtCl₄ using polarized light show that the 25,500 cm.⁻¹ band occurs in x, y and the 30,200 cm.⁻¹ band occurs in z polarization.¹² These polariza-

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tions are expected for the assignments given here, assuming a vibronic intensity giving mechanism. Chatt, Gamlen and Orgel^{2a} previously assigned the spectrum of PtCl_4^{2-} somewhat differently ($17,700 \text{ cm.}^{-1}$, ${}^1A_{1g} \rightarrow {}^3A_{2g}$; $21,000 \text{ cm.}^{-1}$, ${}^1A_{1g} \rightarrow {}^3E_g$; $25,500 \text{ cm.}^{-1}$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$; $30,200 \text{ cm.}^{-1}$, ${}^1A_{1g} \rightarrow {}^1E_g$). However, the $25,500 \text{ cm.}^{-1}$ and the $30,200 \text{ cm.}^{-1}$ bands are both quite sensitive to axial perturbations (both bands shift to the red on changing the solvent from 12 *M* HCl to water).¹³ This is evidence against the assignments of Chatt, *et al.*,^{2a} and is consistent with the assignments proposed here.

The AuCl_4^- and AuBr_4^- complexes do not exhibit any bands which can unambiguously be assigned to *d-d* transitions. In these cases the two charge transfer bands appear at lower energies (than for PtX_4^{2-} complexes) and mask the weaker *d-d* bands.

The only bands which can clearly be identified in the cyanide complexes are due to charge transfer transitions. A rough calculation may be performed to show that the charge transfer bands in $\text{Ni}(\text{CN})_4^{2-}$ appear at about the energy expected for transitions from metal *d*-orbitals to the ligand $a_{2u}(\pi^*)$ orbital. The ionization potential of HCN is about 14 e.v.¹⁴ The calculated separation of the single electron π^b and π^* levels in HCN is 9 e.v.¹⁵ Thus the coulomb energy of the π^* level of complexed CN^- may be estimated at -5 e.v. The coulomb energy of the Ni^{2+} *d*-orbitals in $\text{Ni}(\text{CN})_4^{2-}$ may be estimated at about -10 e.v. , using the spectroscopic data compiled by Moore,²⁴ and assuming that the net charge on the complexed Ni^{2+} is actually about $+1$. This leaves 5 e.v. , or about $40,000 \text{ cm.}^{-1}$, as the difference in energy of the single electron *d* (Ni^{2+}) and $\pi^*(\text{CN}^-)$ orbitals. Since the $a_{2u}(\pi^*)$ level is stabilized by the empty $4p_z$ metal orbital (also by $+2\beta(v,v)$) and since the $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ and $3d_{z^2}$ orbitals are actually weakly antibonding, the appearance of the three charge transfer bands in $\text{Ni}(\text{CN})_4^{2-}$ between $32,900 \text{ cm.}^{-1}$ and $37,500 \text{ cm.}^{-1}$ is in accord with theory.

The separation Δ_1 for the cyanide complexes is by far the largest of the three orbital parameters, and illustrates that the $d_{x^2-y^2}$ is much more strongly antibonding than any of the other *d*-orbitals. The separation Δ_3 decreases regularly in going from Ni^{2+} to Pt^{2+} (for $\text{Ni}(\text{CN})_4^{2-}$ and $\text{Pd}(\text{CN})_4^{2-}$, the d_z is more unstable than d_{xz} , d_{yz} ; for $\text{Pt}(\text{CN})_4^{2-}$, the d_z is more stable than d_{xz} , d_{yz}). This is compatible with the idea that the axial interaction of the water molecules in water solution decreases in going from Ni^{2+} to Pt^{2+} . The two components observed for the intense charge transfer band in $\text{Pt}(\text{CN})_4^{2-}$ are consistent with its assignment as ${}^1A_{1g} \rightarrow {}^1E_u$; the 1E_u excited state is expected to be split by second-order spin-orbit effects.

The assignments given in this paper for the cyanide complexes differ considerably with assignments given by other investigators.^{4,5,7} The reason for this disagreement is found in our "band assignment philosophy"—assign only the bands which can clearly be identified as to energy and intensity. In the case of the cyanide complexes these bands are almost certainly due to charge transfer transitions, as judged by their large intensities.

A careful comparison of the charge transfer bands for the PtCl_4^{2-} , AuCl_4^- , $\text{Pt}(\text{CN})_4^{2-}$ and $\text{Au}(\text{CN})_4^-$ complexes offers further proof of the assignments given here. Thus the first charge transfer band appears at lower energy for AuCl_4^- than for PtCl_4^{2-} , as expected for a ligand \rightarrow metal type electronic transition, since Au^{3+} is a better electron acceptor than Pt^{2+} . On the

other hand, the first charge transfer band for $\text{Au}(\text{CN})_4^-$ occurs at *higher energy* than for $\text{Pt}(\text{CN})_4^{2-}$, expected only if the charge transfer for these cyanide complexes is of the metal \rightarrow ligand type.

The charge transfer band systems observed for the halide (case 1) and cyanide (case 2) complexes should serve as a guide in assigning the charge transfer in other square planar complexes as ligand (π) \rightarrow metal (case 1) or metal \rightarrow ligand [$a_{2u}(\pi^*)$] (case 2). In the halide complexes the two charge transfer bands are separated by $10,000$ to $13,000 \text{ cm.}^{-1}$. Thus it can be estimated that the $b_{2u}(\pi)$ and $e_u(\pi^b)$ molecular orbitals are separated by at least $10,000 \text{ cm.}^{-1}$ in a typical square planar complex. This is a reasonable value since the b_{2u} orbital is non-bonding with a ligand interaction of $-2\beta(v,v)$, and the e_u orbital is π -bonding.²⁵

The three charge transfer bands due to metal \rightarrow ligand [$a_{2u}(\pi^*)$] transitions and exhibited by the cyanide complexes are much more closely spaced. The two orbitally allowed metal \rightarrow ligand transitions ($a_{1g}(\sigma^*) \rightarrow a_{2u}(\pi^*)$, $e_g(\pi^*) \rightarrow a_{2u}(\pi^*)$) are only $2,000$ – $3,000 \text{ cm.}^{-1}$ apart in all the cyanide complexes, since the $a_{1g}(\sigma^*)$ and $e_g(\pi^*)$ metal orbitals are virtually non-bonding and thus very nearly equal in energy in these complexes.

Thus these two types of charge transfer show quite different properties and should be distinguishable in other nd^8 square planar complexes. The ligand (π) to metal type will have two bands, spaced by about $10,000 \text{ cm.}^{-1}$, the second more intense than the first. The metal \rightarrow ligand [$a_{2u}(\pi^*)$] type will have three closely spaced bands with intensities $b_{2g}(\pi^*) \rightarrow a_{2u}(\pi^*)$ [small], $a_{1g}(\sigma^*) \rightarrow a_{2u}(\pi^*)$ [intermediate] and $e_g(\pi^*) \rightarrow a_{2u}(\pi^*)$ [large]. The exact positions of these bands give of course the best clues to the relative ordering of the *d*-orbital energy levels. In all probability there will be cases in which the $b_{2g}(\pi^*)$ level is fairly close to $a_{1g}(\sigma^*)$ and $e_g(\pi^*)$ (Δ_2 small), and thus only the two orbitally allowed bands will be observed. In any event the spacing of the two orbitally allowed charge transfer bands will easily distinguish between ligand \rightarrow metal and metal \rightarrow ligand type transitions for the nd^8 square planar complexes.

The "ring" diamagnetism apparently observed for $\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ may be considered as experimental evidence of electron delocalization through the cyanide system. The electrons in the $a_{2u}(\pi^b)$ orbital, in particular, would be expected to generate considerable "ring current."

Experimental.—The complex $\text{K}_2\text{Ni}(\text{CN})_4 \cdot \text{H}_2\text{O}$ was prepared as described in the literature.²³ The electronic spectral measurements were made using a Cary 14 spectrophotometer.

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Hexachlorometallates of Trivalent Chromium, Manganese and Iron

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Compounds containing hexachlorometallate ions of trivalent chromium, manganese, and iron have been prepared by stabilizing the anion in a crystal lattice with the tris-(1,2-propanediamine)-cobalt(III) cation. The existence of the complex anions has been proved by isomorphism with salts of known hexachlorometallate(III) ions and the same cation, and by X-ray data obtained from single crystals of $[\text{Co}(\text{C}_3\text{H}_7\text{N}_2)_3][\text{FeCl}_6]$. Magnetic data showed that the ground state of these compounds is the expected high-spin state. Dq values of 1318, 1754 and 920 cm^{-1} for $[\text{CrCl}_6]^{3-}$, $[\text{MnCl}_6]^{3-}$ and $[\text{FeCl}_6]^{3-}$, respectively, were determined from spectral data.

Introduction

Complex ions including those not found in appreciable concentrations in solution often can be stabilized in a crystal lattice providing that the energetics of formation of the complex ion from solvated species is not too unfavorable relative to the lattice energy. A good guide to a suitable counter ion is the rule that the lattice energy usually is largest for ions of equal and opposite charge. Furthermore, a counter ion of similar size is best since disparate sizes promote solvation.

This approach has been used recently by Gill and Nyholm,¹ who have isolated stable compounds containing such ions as the tetrahalonickellate(II) ion. Similarly, Mori² has prepared a number of chlorocuprates by stabilizing the complex anions in a lattice with the hexamminechromium(III) cation.

Although there are several references in the older literature to compounds having stoichiometries consistent with hexachlorometallate salts for trivalent first transition series elements, e.g., Ti_3CrCl_6 ,³ $\text{Cs}_3\text{FeCl}_6 \cdot \text{H}_2\text{O}$,⁴ and $(\text{NH}_4)_3\text{CrCl}_6$,⁵ the properties of the complex anions are unknown. In fact, evidence reported here casts doubt on the existence of any hexachlorometallate ions in these compounds. We now wish to report the preparation and some physical properties of compounds which do contain hexachlorometallate ions of trivalent chromium, manganese, and iron. Up to now the position of the chloride ion in the neuphel-auxetic series has been based on spectral studies of anhydrous chromium(III) chloride and complexes of second and third transition series ions.⁶ Studies on octahedral complexes of first transition series ions coordinated only by chloride should provide additional information concerning the ligand field of the chloride ion.

Experimental

Tris-(1,2-propanediamine)-cobalt(III) Hexachlorochromate(III).—A small amount of the pink compound crystallized from a concentrated hydrochloric acid solution (50 ml.) of chromium(III) chloride hexahydrate (5.4 g., 0.020 mole) and tris-(1,2-propanediamine)-cobalt(III) chloride (3.8 g., 0.010 mole) after standing for several days. The crystals were collected on a Büchner funnel, washed well with water, then with alcohol and ether, and dried in an oven at 110° for four days.

Anal. Calcd. for $\text{CoC}_9\text{H}_{30}\text{N}_6\text{CrCl}_6$: C, 19.80; H, 5.53; N, 15.40. Found: C, 19.87; H, 5.61; N, 15.09.

Tris-(1,2-propanediamine)-cobalt(III) Hexachloromanganate(III).—This compound was precipitated from a hot solution of manganese(II) sulfate monohydrate (3.4 g., 0.020 mole) and

tris-(1,2-propanediamine)-cobalt(III) chloride (7.6 g., 0.020 mole) in a minimum amount of hydrochloric acid by the addition of small amounts of sodium chlorate. The dark brown compound was collected on a Büchner funnel, washed with alcohol, acetone, and ether, and dried in an evacuated desiccator over potassium hydroxide. The yield was 8.1 g. (75%).

Anal. Calcd. for $\text{CoC}_9\text{H}_{30}\text{N}_6\text{MnCl}_6$: C, 19.70; H, 5.50; N, 15.31; Cl, 38.72. Found: C, 20.18; H, 5.61; N, 15.24; Cl, 38.98.

The compound decomposed slowly upon standing presumably evolving chlorine. The magnetic moment of a sample that had been stored for three months was 0.3 B.M. higher than that of a freshly prepared sample.

Tris-(1,2-propanediamine)-cobalt(III) Hexachloroferrate(III).—A solution of iron(III) chloride hexahydrate (2.7 g., 0.010 mole) in 5 ml. of hot water was added to a solution of tris-(1,2-propanediamine)-cobalt(III) chloride (3.8 g., 0.010 mole) in 10 ml. of hot water. The solution was evaporated to about half the original volume. A few milliliters of concentrated hydrochloric acid was added; the yellow crystals formed were collected on a Büchner funnel, washed with alcohol, acetone, and ether, and air dried. The compound was recrystallized from hot water with the addition of hydrochloric acid. The yield was 1.8 g. (29%).

Anal. Calcd. for $\text{CoC}_9\text{H}_{30}\text{N}_6\text{FeCl}_6$: C, 19.66; H, 5.50; N, 15.28; Cl, 38.69. Found: C, 19.88; H, 5.14; N, 15.46; Cl, 38.69, 38.61.

Tris-(1,2-propanediamine)-cobalt(III) Hexachloroindate(III).—This compound was prepared as was the corresponding iron compound. The yield was 87%.

Anal. Calcd. for $\text{CoC}_9\text{H}_{30}\text{N}_6\text{InCl}_6$: C, 17.76; H, 4.96; N, 13.81; Cl, 34.96. Found: C, 17.68; H, 5.00; N, 13.08; Cl, 35.00.

Tris-(1,2-propanediamine)-rhodium(III) Hexachlorometallates(III).—Compounds with the tris-(1,2-propanediamine)-rhodium(III) cation were prepared by the methods described above. The analytical data for the new compounds are given in Table I.

Hexaamminecobalt(III) Hexachloroferrate(III).—A solution of ferric chloride hexahydrate (1.4 g., 0.005 mole) in 10 ml. of hot water was added to a hot solution of hexaamminecobalt(III) chloride (0.43 g., 0.0016 mole) in 70 ml. of 3.4 N hydrochloric acid. The resulting solution was heated for a few minutes until an orange product crystallized. The crystals were collected on a Büchner funnel, washed with alcohol and ether and dried in an evacuated desiccator over potassium hydroxide. The yield was 0.5 g. (72%).

Anal. Calcd. for $\text{CoN}_6\text{H}_{18}\text{FeCl}_6$: N, 19.54; H, 4.18; Cl, 49.55. Found: N, 19.52; H, 4.13; Cl, 48.42.

The preparation could not be made at room temperature because of the insolubility of hexaamminecobalt(III) chloride in a solution with a chloride ion concentration high enough to facilitate the formation of the hexachloroferrate(III) ion. Detailed studies of this compound were not undertaken because we experienced difficulties in preparing the corresponding manganese compound.

Experiments with Other Cations and Anions.—Proper conditions could not be found for the preparation of hexachloroferrate(III) salts of the tris-(2,3-butanediamine)-cobalt(III) or tris-(1,2-cyclohexanediamine)-cobalt(III) cation. An orange product crystallized from a solution of tris-(ethylenediamine)-cobalt(III) chloride and ferric chloride after a few days. The crystals were collected on a Büchner funnel, washed with alcohol and ether, and dried in air.

Anal. Calcd. for $\text{CoC}_6\text{H}_{24}\text{N}_6\text{FeCl}_6 \cdot 1.5\text{H}_2\text{O}$: C, 13.48; H, 5.08; N, 15.74. Found: C, 13.21; H, 4.68; N, 15.92.

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