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TRANSITION METAL CHEMISTRY

A Series of Advances

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TRANSITION METAL
CHEMISTRY

Volume 1

Introduction to the Series

This series of comprehensible reviews and monographs at the research level is devoted to the science of those substances commonly called the transition elements. Transition metal chemistry is one of the oldest and largest areas of research in inorganic chemistry, and the many facets of its progress will be surveyed regularly. Other, newer areas of transition metal physics and transition metal biology also will be reviewed, for it is in these areas that some of the more important future discoveries are going to be made. While the choice of the articles reflects the interests of the editor and the contributing authors, it is hoped that the coverage over a number of volumes will present a broad enough view of the field to satisfy all. Interested contributors are invited to contact the editor.

The editor is most grateful to the distinguished scientists who have contributed articles to these volumes and hopes that the scientific community will find the authors' efforts to have been well worthwhile.

R.L.C.

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Chapter 1

Electronic Structure and Stereochemistry of Cobalt(II)

RICHARD L. CARLIN

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I. INTRODUCTION

In this review we plan to survey some of the recent literature on the coordination chemistry of divalent cobalt. Emphasis will be centered on the correlation of molecular structure and stereochemistry with electronic structure as derived particularly from spectral and magnetic measurements. We list in the several tables reference to various metal-ligand systems, and the text will attempt to bring together the theoretical bases for interpretation of the experimental results. The only previous reviews devoted to this topic are those of Busch[1] and Lewis.[2] Neither of these reviews is complete, nor can this one be, for much of the older literature is not discussed here nor much of the interesting work peripheral to the central problem.

Any reviewer dealing with topics in ligand field theory must not only record his debt to the fine book by Ballhausen[3] and the equally fine review by McClure,[4] but must also call attention to these useful works for both the background of this paper and for additional surveys of the literature.

The cobalt(II) ion, which has seven *d* electrons, is best known in four-coordinate tetrahedral and six-coordinate octahedral stereochemistries. Since the coordination sphere of the ion is labile, the equilibrium distribution of ligands is rapidly reached in solution. No case of geometrical isomerism has yet been reported for this ion.

The factors which determine the particular stereochemistry obtained by cobalt are not yet understood, but work in progress in many laboratories may soon indicate some of the factors. Thus, the equilibrium

$$\underset{\text{Tetrahedral}}{\mathrm{Co\ py_2X_2}} + 2\mathrm{py} \rightleftharpoons \underset{\text{Octahedral}}{\mathrm{Co\ py_4X_2}}$$

studied in nonaqueous solution has been investigated by Katzin[5] and more recently by Nelson et al.[6] Systems of this sort enable one to examine, among other factors, steric effects and the polarizability of the ligands; these last two effects are frequently impossible to separate.

The magnitude of the problem may be realized by considering the series of crystalline complexes, Co py_2X_2 (X = Cl, Br, I, NCS).[7] The chloride exists in two forms, a pink octahedral stable isomer and a blue tetrahedral unstable modification. Both the bromide and iodide form only the tetrahedral structure, but the pseudohalide thiocyanate forms only an octahedral complex. An obvious point to wonder about is how much the precipitation from solution of a crystalline complex influences the choice of geometry.

Recent work on ethylenethiourea[8] as a ligand showed that cobalt halides add two moles of ethylenethiourea to form the tetrahedral molecules, $[Co(etu)_2X_2]$. However, with bidentate dimethylmercaptoethane as donor,[9] two moles of ligand add to the cobalt halides to form the octahedral complexes, $[Co(CH_3SCH_2CH_2SCH_3)_2X_2]$. It is difficult to learn why the complexes differ in the stereochemistries they assume, unless the cause is simply due to the entropy effects associated with the bidentate ligand.

An interesting problem is raised by the recent discovery of a series of nitrate complexes.[10–15] The nitrate ion, as shown by the complete crystal structure analysis[13] of $[Co(Me_3PO)_2(NO_3)_2]$, may be bidentate, and the molecular environment of the cobalt in the latter compound is best described only as distorted. Yet, the spectral and magnetic properties of the complex led it originally to be assigned to a tetrahedral structure.[10] The

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ability of bidentate nitrate to cause the metal ion to consider it as a monodentate ligand has been discussed.[14]

Since a doublet state from ^2G becomes the ground state in strong octahedral fields, it would be very interesting to find a compound with a ligand field strength very close to the cross-over point. Such a compound appears to be the bis(2,6-pyridindialdihydrazone) of cobaltous iodide, which exhibits a strongly temperature dependent magnetic moment. Although a complete crystal structure analysis is necessary to substantiate the claim, the observed magnetic behavior may be understood by postulating a doublet (1.9 B.M.)–quartet (5.2 B.M.) equilibrium.[16]

II. STRUCTURE

The most common geometries for the cobaltous ion are four-coordinate tetrahedral and six-coordinate octahedral. These are, however, idealized geometries for few, if any, complexes have been shown to attain symmetry high enough to be called either tetrahedral or octahedral in the group-theoretical sense. The $[CoCl_4]^{2-}$ anion, for example, has angles of 107° 20′, 108° 50′, 109° 20′, and 116° 20′ in Cs_2CoCl_4; what is more, the angles vary with the cation present. In $[Me_4N]_2(CoCl_4)$, the angles are 108° 18′, 109° 6′, 110° 24′, and 111° 42′.

Furthermore, true cubic symmetry is lost immediately when more than one type of ligand enters the coordination sphere. Typical examples would be the tetrahedral $[Co\ py_2Cl_2]$ and the octahedral $CoCl_2 \cdot 2H_2O$, which attains an octahedral geometry by bridging chloride ions.

To be accurate, we should preface the terms "tetrahedral" and "octahedral" by the prefix "pseudo," or at least leave the words in quotes. While, for convenience, we shall not do this, the reader should keep the distinction in mind.

A list of all the crystal structures of cobaltous compounds which have been determined may be found in Table 1. Cobalt is eight-coordinate in $(As\phi_4)_2Co(NO_3)_4$, $C2/c$; $(As\phi_4)_2Co(O_2CCF_3)_2$ appears similar, $I4_1/a$. Red, diamagnetic $[Co_2(CNMe)_{10}](ClO_4)_4$, $P2_12_12$, contains dimers.[16a]

III. SPECTRA

The electronic spectra of cobalt(II) in its various stereochemistries are now quite well known, and several generalizations can readily be made. Briefly, with relatively simple ligands, the spectrum of tetrahedral cobalt is more intense than that of octahedral cobalt (factor of 10^2 in extinction coefficient), and is characterized by a more strongly structured peak in the

TABLE 1

Crystal Structures

Compound	Space group	Comments	Ref.
1. Octahedral and Related Structures			
$CoCl_2 \cdot 2H_2O$	$C2/m$	Polymeric; Cl bridge	a
$CoCl_2 \cdot 6H_2O$	$C2/m$	*trans*-$[Co(OH_2)_4Cl_2]$	b
$CoSO_4 \cdot 6H_2O$	$C2/c$	$Co(OH_2)_6^{2+}$	c
$[Co(H_2O)_6][GeF_6]$	$P2_1/a$	CsCl type	d
$Co(OAc)_2 \cdot 4H_2O$	$P2_1/c$		e
CoF_2	$P4/mnm$	Rutile type	f
$KCoF_3$	$Pm3m$	Cubic	g
$Co(AlCl_4)_2$	$I2/c$	Polymeric	h
$Coacac_2 \cdot 2H_2O$	$P2_1/c$	Trans	i
$[Co(Me_3PO)_2(NO_3)_2]$	$P2_1/c$	Irregular	j
$[Co\ py_2Cl_2]$	$P2/b$	Polymeric	k
$[Co\ py_4Cl_2]$	$I4_1/acd$	Trans	l
$[Co\ py_4Br_2]$	Pna(?)	Trans	m
$[Co\ py_2(NCS)_2]$	$C2/m$	NCS-bridge	n
$[Co\ py_4(NCS)_2]$	$C2/c$ or Cc	Co-NCS linear	o
$[Co\ thiourea_2(NCS)_2]$	$P\bar{1}$	Polymeric; thiourea bridge	p
2. Tetrahedral Structures			
Cs_2CoCl_4	$Pnam$	Distorted $CoCl_4^{=}$	q
$(Me_4N)_2CoCl_4$	$Pnma$		r
Cs_3CoCl_5	$I4/mcm$	Distorted $CoCl_4^{=}$	s
$HgCo(NCS)_4$	$I\bar{4}$		t
$K_2Co(NCS)_4 \cdot 4H_2O$	$P2_122_1$	No change on losing H_2O	u
$Na_2Co(NCS)_4 \cdot 8H_2O$	$P\bar{4}$ or $P4_2/n$	Mineral	v
$[Co(NH_3)_4](ReO_4)_2$	$F\bar{4}3m$	Isomorphous with tetrahedral Cd complex	w
$[Co(p\text{-toluidine})_2Cl_2]$	$I2/a$	Similar molecules	x
$[Co(p\text{-toluidine})_2I_2]$	$Fdd2$		y
$[Co(dipivaloylmethane)_2]$	$I4_1/a$	Metal atom at $\bar{4}$	z

---

[a] B. K. Vainstein, *Dokl. Akad. Nauk SSSR 68*, 301 (1949); B. Morosin and E. J. Graeber, *Acta Cryst. 16*, 1176 (1963).

[b] J. Mizuno, *J. Phys. Soc. Japan 15*, 1412 (1960).

[c] A. Zalkin, H. Ruben, and D. H. Templeton, *Acta Cryst. 15*, 1219 (1962).

[d] T. S. Khodashova, *Soviet Phys.-Cryst. 2*, 602 (1957).

[e] J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst. 6*, 609 (1953).

[f] J. W. Stout and S. A. Reed, *J. Am. Chem. Soc. 76*, 5279 (1954).

[g] K. Knox, *Acta Cryst. 14*, 583 (1961).

[h] J. A. Ibers, *Acta Cryst. 15*, 967 (1962).

[i] G. J. Bullen, *Acta Cryst. 12*, 703 (1959).

[j] F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc. 85*, 2402 (1963).

[k] J. D. Dunitz, *Acta Cryst. 10*, 307 (1957).

[l] M. A. Porai-Koshits, *Proc. Inst. Cryst. Acad. Sci. USSR 10*, 288 (1954).

[m] A. S. Antsyshkina and M. A. Porai-Koshits, *Soviet Phys.-Cryst. 3*, 684 (1958).

[n] M. A. Porai-Koshits and G. N. Tishchenko, *Soviet Phys.-Cryst. 4*, 216 (1960).

[o] M. A. Porai-Koshits and A. S. Antsyshkina, *Soviet Phys.-Cryst. 3*, 694 (1958).

[p] M. Nardelli, A. Braibanti, and G. Fava, *Gazz. Chim. Ital. 87*, 917, 1209 (1957).

[q] M. A. Porai-Koshits, *Kristallografiya 1*, 291 (1956).

[r] B. Morosin and E. C. Lingafelter, *Acta Cryst. 12*, 611 (1959).

[s] H. M. Powell and A. F. Wells, *J. Chem. Soc. 1935*, 359; B. N. Figgis, M. Gerloch, and R. Mason, *Acta Cryst. 17*, 506 (1964).

[t] J. W. Jeffrey, *Nature 159*, 610 (1947).

[u] G. S. Zhdanov and Z. V. Zvonkova, *Zh. Fiz. Khim. 24*, 1339 (1950).

[v] A. Preisinger, *Mineral. Petrog. Mitt. 3*(3), 376 (1952–53).

[w] K. Pitzer, *Z. Krist. 92*, 131 (1935).

[x] T. I. Malinovskii, *Soviet Phys.-Cryst. 2*, 723 (1957).

[y] T. I. Malinovskii, *Soviet Phys.-Cryst. 3*, 365 (1958).

[z] F. A. Cotton and J. S. Wood, *Inorg. Chem. 3*, 245 (1964).

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visible region (Fig. 1). Unfortunately, both environments give rise to bands in the same position-around 20,000 cm^{-1}, although tetrahedral compounds more frequently exhibit maxima near 15,000 cm^{-1}. Certainly the best spectral indicator of stereochemistry is the intensity, when the spectrum is not complicated by overlap with a strong U-V (charge transfer) tail.

Color is *not* a useful criterion of stereochemistry. While many octahedral compounds are indeed "pink" or "brick red," and many tetrahedral compounds are "blue," several contradictory examples are well-documented. Thus, Co_2SiO_4 is purple and octahedral[17b] and Co dipivaloylmethanide is pink and tetrahedral.[18]

So few compounds have been shown definitively to contain square-planar Co(II) that no empirical correlation of spectra with this geometry is available.

The most careful theoretical exploration of the spectra of cobalt is due to Liehr.[19] This important paper presents the results of a complete calculation of the energy with respect to the ligand field coulombic (Dq), spin-orbit (λ), and electron correlation parameters (Racah's B and C) for octahedral and tetrahedral cobalt(II) [and also chromium(III)]. The results have been presented in graphic form. Liehr points out immediately the weaknesses in the method, and the paper is warmly recommended to those who believe that simple ligand field theory will answer all the questions of transition metal chemistry.

The method used to calculate energy levels is the Slater-Condon-Shortley procedure. This method does not lead to an accurate calculation of all of the atomic energy levels—*even in the free* (*gas-phase*) *ion*—and so the calculations concerning complexes can be no better than the method. Second, even the most complete ligand field calculations are still simple and qualitative in that they are not complete molecular orbital calculations. While many attempts have been made in this direction recently, we are

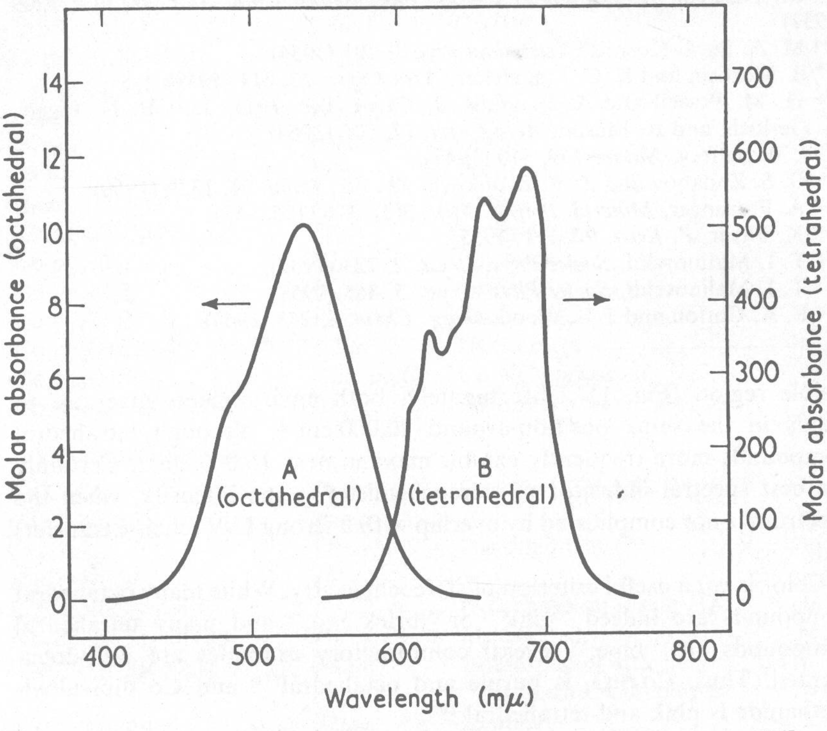

Fig. 1. The visible spectra of $[Co(H_2O)_6]^{2+}$ (curve *A*) and $[CoCl_4]^{2-}$ (curve *B*).[17a]

still, for example, quite some time away from taking proper account of the influence of charge transfer states.

Before discussing the complete calculations of Liehr and several of the applications,[20,21] it may be well to outline a simple approach to the spectra of cobalt(II).

Consider first (Fig. 2) the energy level diagram for tetrahedral cobalt. Three electronic transitions are depicted from the ground state, $^4A_2$. The first, ν_1, occurs at an energy of $10Dq$, and since this band should occur in the 3000–5000 cm^{-1} region for most complexes, it has been little observed. On the other hand, few investigators have even searched for it, and it seems that more effort in this direction might be profitable. Near infrared spectra of tetrahedral cobalt(II) are reported in reference 21a.

The band corresponding to ν_2 is usually broad and appears in the near infrared; ν_3 is intense, broad, and usually exhibits a great deal of structure. The blue color frequently characteristic of tetrahedral cobalt is due to this band, which usually occurs in the 15,000–20,000 cm^{-1} region. Representative spectra for the tetrahedral tetrahalo cobalt complexes are displayed in Figure 3.

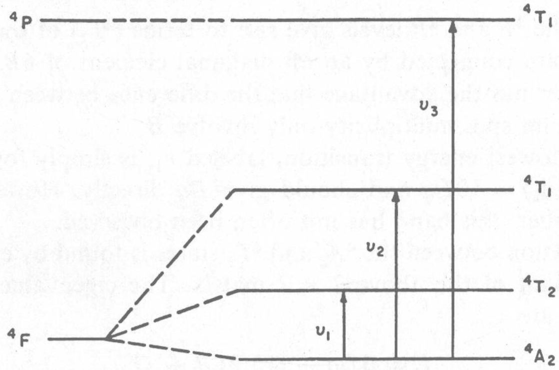

Fig. 2. Simplified energy level diagram for tetrahedral d^7.

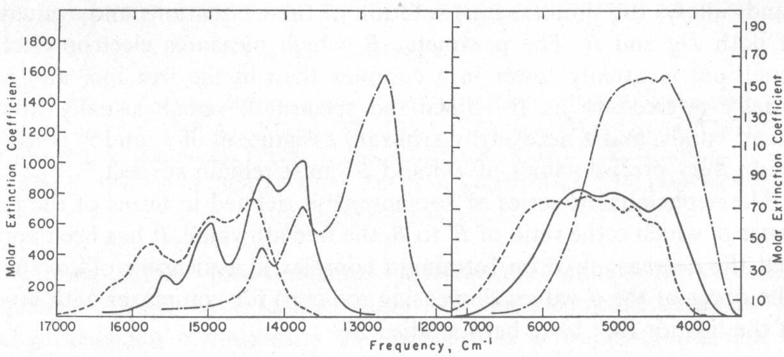

Fig. 3. Spectra of the $(n\text{-Bu}_4\text{N})_2[\text{CoX}_4]$ salts: (- -), X = Cl; (——), X = Br; (- ·), X = I.[25]

For the uninitiated, we shall now show how the above energy level diagram is derived and how the spectral parameters Dq and B may be derived from the spectra. The information is derived[22] from the matrices of Tanabe and Sugano,[23] which are

$$\begin{array}{rl} {}^4A_2(F): & -12Dq - 15B \\ {}^4T_2(F): & -2Dq - 15B \\ {}^4T_1(F), {}^4T_1(P): & \begin{vmatrix} -2Dq - 3B & 6B \\ 6B & 8Dq - 12B \end{vmatrix} \end{array}$$

Since both the ^4F and ^4P levels give rise to terms ($^4T_1$) of the same symmetry, they are connected by an off-diagonal element of $6B$. The use of this parameter has the advantage that the difference between levels of the same maximum spin multiplicity only involve B.

Now, the lowest energy transition, labeled ν_1, is simply found as $\nu_1 = E(^4T_2) - E(^4A_2) = 10Dq$ and should give Dq directly. However, as was indicated earlier, this band has not often been observed.

The separation between the $^4A_2$ and $^4T_1$ states is found by evaluation of the determinant of the above 2×2 matrix. The eigenvalues, E, of the determinant are

$$E = 3Dq - (15/2)\,B \pm Q$$

where $Q = (1/2)\,[(-6Dq + 15B)^2 + 64(Dq)^2]^{\frac{1}{2}}$. Then $\nu_2 = E[^4T_1(F)] - E(^4A_2) = 3Dq - (15/2)B - Q + 12Dq + 15B = 15Dq + (15/2)B - Q$ and $\nu_3 = 15Dq + (15/2)\,B + Q$. Observation and assignment of the two bands allows the simultaneous solution of these equations and evaluation of both Dq and B. The parameter B, which measures electron-electron repulsion, is usually lower in a complex than in the free ion, and so is usually referred to as B'. Since the spectra of cobalt usually involve broad bands, and a necessarily arbitrary assignment of ν_2 and ν_3 is usually made, very precise values of Dq and B' must remain suspect.[20]

The nephelauxetic series of Jørgensen[24] is defined in terms of the parameter β, which is the ratio of B' to B, the free ion value. It has been argued that the decrease in B on forming a complex is a measure of covalency. The order of the β values (increasing ionicity) for complexes with several of the ligands that have been studied is[25]

$$\text{etu} \sim \text{I}^- \sim \text{N}_3^- < -\text{NCS} \sim \text{Br}^- \sim \text{Cl}^- \sim -\text{NCO}^- < \text{OH}^- < \phi_3\text{PO}$$

where etu is ethylenethiourea, a sulfur donor.[8] It will be noticed that this order roughly parallels the polarizability of the donor atom.

It has also been suggested[18] that there is a correlation between absorption band intensities and the amount of lowering, ΔB, of the B value from the free cobalt(II) ion value. The intensities of the spectral bands of tetrahedral complexes have been shown[26] to be due in large part to molecular orbital mixing (i.e., covalency). Therefore covalency, as represented by the nephelauxetic parameter β, and the intensity, as measured by the

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