THE CHEMISTRY OF THE METAL OXALATO COMPLEXES

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I. INTRODUCTION

Several textbooks and review articles devoted to the chemistry of coördination compounds (27, 37, 39, 50, 112, 256, 274, 409) contain scattered material on the oxalato complexes. No specific review of these complexes is presently available, although *oxalate* as a bidentate ligand has been of great interest in coördination chemistry for a long time. It is the purpose of the present review to collect most of the pertinent details concerning the chemistry of the oxalato complexes of metals, in the hope of encouraging increased attention to the structure, stability, and lability of these interesting compounds. The literature survey includes published work through 1959.

II. OXALIC ACID AND THE SIMPLE OXALATES

A. OCCURRENCE

Oxalic acid, one of the oldest known acids, was discovered by Scheele nearly 200 years ago and is biologically, chemically, and industrially important. It is widely distributed in nature, such as in certain wild species of genera *Rumex* and *Xanthoxalis: Rumex acetosella, Rumex acetosa, Xanthoxalis stricta, Oxalis acetosella, Sarcobatus vermiculatus.* Air-dried leaves of the latter contain as high as 9.4 per cent of oxalic acid as the neutral sodium and potassium salts (89). A detailed account of the occurrence of organic acids (in particular of oxalic acid) in plants is available in a bulletin of the United States Department of Agriculture (62). Certain types of algae, moulds, lichen, and ferns are rich in oxalic acid, and the urine of animals and man generally contains calcium oxalate, particularly in pathological cases (oxaluria). Ferrous and calcium oxalates are sometimes found as minerals.

B. PREPARATION AND PROPERTIES

Oxalic acid is made by a variety of methods and its physical and chemical properties are well known (174, 279). Interest in the study of inorganic oxalates has resulted largely from the use of oxalate ion as a precipitating and a chelating agent. Most of the simple oxalates are insoluble in water (excepting those of the alkali metals) and are therefore prepared generally by precipitation reactions of the following type:

$$M^{n+}_{aq} + n/2\ C_2O_4^{2-} \rightarrow M(C_2O_4)_{n/2}\cdot xH_2O$$

Sodium oxalate is commercially made from the cellulose of sawdust by fusion with alkali and decomposition of the resulting formate to yield the oxalate. It is also obtained by the reaction of carbon dioxide with sodium amalgam. Oxalates of potassium, rubidium, and cesium are prepared in a like manner.

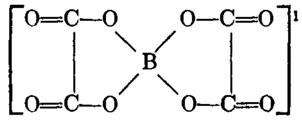
Oxalates of lithium, sodium, potassium, rubidium, cesium, and ammonium are soluble in water, lithium oxalate being the least soluble; there is no evidence of any complexation in any of these cases.

Beryllium oxalate has the formula $BeC_2O_4\cdot 3H_2O$ and is highly soluble in water, unlike the other oxalates of elements of Group IIA. This high solubility is assumed to be a case of autocomplexation when solid beryllium oxalate is dissolved in water:

$$2BeC_2O_4 = Be^{2+} + Be(C_2O_4)_2^{2-}$$

A salt of the formula $Na_2Be(C_2O_4)_2\cdot 2H_2O$ has been prepared, supporting the concept of the $Be(C_2O_4)_2^{2-}$ ion (386).

Boron forms an interesting oxalate in which all bonds are reported to be covalent (112):



Because of the coördinating properties of the bidentate oxalate ion, most of the metals form complex oxalates in addition to simple oxalates. However, only complex oxalates are indicated for the metals titanium, niobium, tantalum, molybdenum, tungsten, osmium, iridium, and antimony, and the existence of simple oxalates of these metals is questionable. Figure 1 summarizes data on the tendency of metals to form oxalates, simple and/or complex.

Many of the simple oxalates are crystalline solids or amorphous powders, white or colored depending on the cation, and are generally sparingly soluble in water. The solubility product constants range from $\sim 10^{-4}$ to $\sim 10^{-30}$; those of the bivalent metal oxalates generally lie between $\sim 10^{-5}$ and $\sim 10^{-15}$. The least soluble oxalates are those of thorium and the rare earths. However, all oxalates dissolve in acids and most of them in excess oxalate to form complexes.

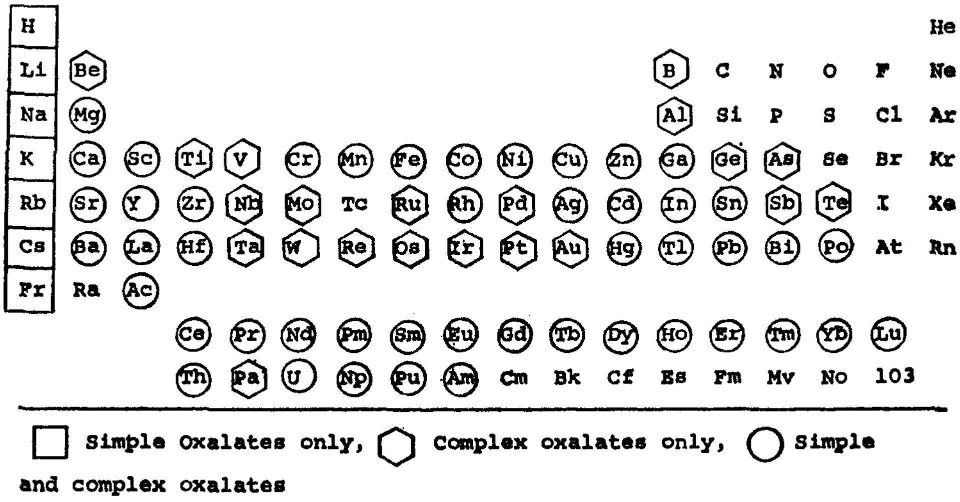


FIG. 1. Metal oxalates.

Since the majority of the simple oxalates are insoluble in water and can be conveniently precipitated, the phenomenon of coprecipitation has been studied in detail, especially in the case of oxalates of calcium, strontium, barium, copper, silver, zinc, cadmium, lead, iron, bismuth, thorium, and the rare earths. The precipitation of $CaC_2O_4 \cdot H_2O$ provides an interesting example from the analytical point of view, as this compound was once suggested as suitable for the gravimetric determination of calcium. Detailed investigation (360) of its hygroscopic character, of the decomposition of the hydrate on prolonged drying at 115–125°C., and of the entrainment properties, however, virtually ruled out its utility for direct weighing. The coprecipitation of anions with calcium oxalate decreases in the order: $IO_3^- > CrO_4^{2-}, SO_4^{2-} > BrO_3^- > Cl^-, Br^-, I^-$. Homogeneous precipitation of oxalate has certain advantages, and calcium, magnesium, zinc, thorium, actinium, uranium(IV), and the rare earths have been successfully determined by this method (159).

The phenomenon of coprecipitation has received increased attention since the discovery of radiotracers, and the mechanism of such carrying processes (181) is explained in terms of (*1*) isomorphous replacement, (*2*) adsorption, (*3*) anomalous mixed-crystal formation, and (*4*) internal adsorption. Recent tracer investigations on the rare earth oxalates using Y^{91}, Ce^{141}, Nd^{147}, and Yb^{169} provide a great deal of information (136, 359, 428) on the various factors which control coprecipitation with solid solution formation, and on the relationship which exists between distribution coefficients and the solubility products of the precipitated oxalates. Cerium has been shown to form (226) anomalous mixed crystals with lead oxalate. In the case of yttrium, cerium, neodymium, and ytterbium complex formation has been established from studies of the solubility of these oxalates in buffered oxalate solutions (93, 94, 137).

Coprecipitation has been particularly useful in isolating carrier-free Po^{210} on oxalates of calcium, strontium, scandium, and lanthanum (381); Pb^{212} on silver oxalate (141, 304); Ra^{224} on silver oxalate (304); Ac^{228} on lanthanum oxalate (283, 452); Pa^{233} on thorium oxalate (413); and Am(III) on bismuth oxalate (414) or lanthanum oxalate (195).

The coprecipitation of iron(III) oxalate with the oxalates of calcium, strontium, barium, zinc, cadmium, copper, silver, and lead has been studied (321). In the case of barium oxalate the mechanism is mainly the occlusion of the mother liquor in the precipitate and the formation of a complex salt between barium oxalate and iron(III) oxalate. With strontium, zinc, cadmium, copper, silver, and lead oxalates, occlusion in the precipitate is the main mechanism of coprecipitation, whereas with calcium and lead oxalates, photochemical decomposition of iron(III) oxalate also increases the coprecipitation of iron. An interesting relation between solubility of the oxalates cited above and the minimum amount of ferric ion adsorbed has been described in the paper quoted.

The coprecipitation of the oxalates has some practical application in the preparation of solid solutions of metal oxides (for example, oxides of magnesium, manganese, iron, cobalt, nickel, and zinc) by thermal decomposition. The mechanism of such thermolysis reactions has been studied recently (352).

III. The Complex Oxalates

A. GENERAL CLASSIFICATION

The metal oxalato complexes may be classified with respect to the number of oxalate groups coördinated to the metal ion, as shown in table 1. Some doubtful and less important metal oxalato complexes (e.g., $Sn_2(C_2O_4)_7^{6-}$ (445)), and several "mixed" oxalato complexes (i.e., those in which ligands other than oxalate are also present, as in $Co(en)_2C_2O_4^+$, $Pd(NH_3)_2C_2O_4^0$, $IrPyCl_3(C_2O_4)^{2-}$, etc.) have been deliberately omitted from the table. These are not regarded as typical oxalato complexes for the purposes of the present discussion, except in certain cases where the oxalate ligand exhibits its own special properties, such as in oxalate substitution reactions. Certain of these mixed oxalato complexes are therefore discussed in detail in the appropriate sections of this review.

The few neutral complexes that are reported to exist in aqueous solution (e.g., $UO_2C_2O_4^0$ (331), $U(C_2O_4)_2^0$ (170), $VO(HC_2O_4)_2^0$ (456), $CoC_2O_4^0$ (142), $Ga_2(C_2O_4)_3^0$ (365), $Sn(C_2O_4)_2^0$ (109)) are not included in table 1, since the evidence regarding their occurrence is not in every case unequivocal. Those which are known with a reasonable degree of certainty are dealt with later in this review (see Section III,C).

B. STRUCTURE

Evidence concerning the structure of the oxalato complexes has been obtained by means of many physicochemical methods, including electrical conductance measurements, polarography, ion exchange, chromatography, electrophoresis, absorption spectroscopy, magnetic susceptibility measurements, x-ray, crystallography, reaction kinetics, and isotopic exchange.

1. *Evidence from preparative chemistry*

Coördination complexes exhibit various types of isomerism, and preparative chemistry has been in many cases very helpful in identifying the isomers. The bidentate oxalate ligand can occupy only two cis positions in an octahedral structure, since the spanning of the trans position is sterically prohibited. For example, oxalate chelation has been used as a diagnostic tool in determining the cis configuration of $Co(NH_3)_2(NO_2)_4^-$ ion (27), although reliance on this method alone is not always justified.

TABLE 1

Classification of oxalato complexes

Class	Formula of Species	Metal Ion and References		
Ia	$M(C_2O_4)^+$	Al(III) (24, 126) Cr(III) (185, 385) Mn(III) (407)	Fe(III) (22) Y(III) (137) In(III) (403)	Sb(III) (310) Ce(III) (23) Nd(III) (94) Tb(III) (93)
Ib	$M(C_2O_4)^-$	Ag(I) (383) Tl(I) (113)	TiO^+ (398) MoO_2^+ (391)	NpO_2^+ (96, 175)
IIa	$M(C_2O_4)_2^-$	Al(III) (24, 126) Cr(III) (438) Mn(III) (75, 407) Fe(III) (22) Co(III) (7) Ga(III) (126, 365)	Y(III) (137) In(III) (292) Sb(III) (310) Ce(III) (94) Nd(III) (94) Gd(III) (361)	Yb(III) (93) Rh(III) (36) Ir(III) (119) Po(III) (380) Pu(III) (153) Am(III) (300)
IIb	$M(C_2O_4)_2^{2-}$	Be(II) (386) Mg(II) (34) Ca(II) (68) Sr(II) (68) Ba(II) (68) Mn(II) (296) Fe(II) (173)	Co(II) (142) Ni(II) (11, 57) Cu(II) (60a, 348, 349) Zn(II) (60a, 235) Cd(II) (235, 423) Pb(II) (231)	Pt(II) (172) TiO^{2+} (25) VO^{2+} (116, 418) OsO_2^{2+} (446) UO^{2+} (79, 84, 301)
IIc	$M(C_2O_4)_2^{3-}$	NpO_2^+ (175)		
IIIa	$M(C_2O_4)_3^{2-}$	Ge(IV) (133) Ru(IV) (78)	Ir(IV) (102) Th(IV) (449)	Pu(IV) (154)
IIIb	$M(C_2O_4)_3^{3-}$	Al(III) (28) Sc(III) (447) V(III) (330) Cr(III) (92, 436) Mn(III) (73–75) Fe(III) (28)	Co(III) (28) Ga(III) (365) Y(III) (137) Sb(III) (309) Ru(III) (78) Rh(III) (437)	Ir(III) (202) Ce(III) (94) Yb(III) (93) Pu(III) (151) NbO^{3+} (182) TaO^{3+} (182)
IIIc	$M(C_2O_4)_3^{4-}$	Co(II) (142) Ni(II) (363)	Zn(II) (243) UO_2^{2+} (449)	
IVa	$M(C_2O_4)_4^{4-}$	Sn(IV) (110) Zr(IV) (131, 354)	Hf(IV) (131, 435) Th(IV) (171)	U(IV) (272) Pu(IV) (154)
IVb	$M(C_2O_4)_4^{5-}$	Pu(III) (143)		

(a) Cis–trans isomerism

Cis–trans isomerism is observed in certain bisoxalato complexes of metals whose ligancy is six and is illustrated in figure 2. It is interesting to note that the cis and trans isomers differ a great deal in their properties and frequently identification is made from preparative chemistry. A case in point is the well-studied $Cr(C_2O_4)_2(H_2O)_2^-$ ion (98, 184, 438). On the other hand, though ions of the type $M(C_2O_4)_2(H_2O)_2^-$ (where M is aluminum, manganese, iron, rhodium, iridium) would be expected to exhibit cis–trans isomerism, no definite evidence is available at the present time from preparative chemistry.

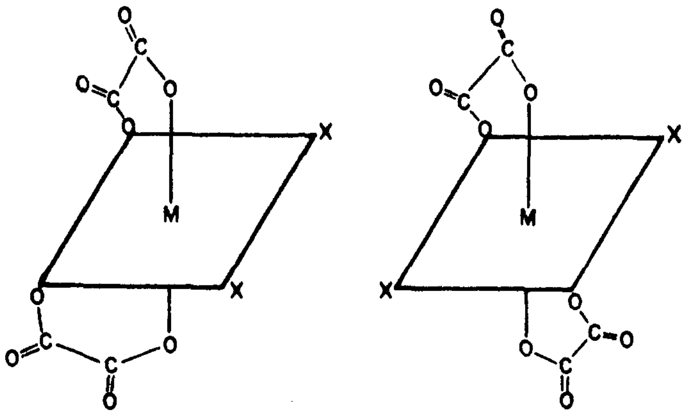


FIG. 2. Cis–trans isomerism in bisoxalato complexes.

Detailed studies of cis–trans isomerism are reported for only a few systems, e.g., $Cr(C_2O_4)_2(H_2O)_2^-$ ion. However, boiling or evaporation to dryness of the cis salt generally yields the trans isomer, e.g., $Ir(C_2O_4)_2Cl_2^{3-}$ (103) and $Rh(C_2O_4)_2Cl_2^{3-}$ (105). Preparative chemistry has been of value in the study of $Mn(C_2O_4)_2(H_2O)_2^-$ (74). The trans compound is golden yellow, whereas the cis is green and the trans–cis isomerization seems to be fast.

In general, cis and trans isomers differ appreciably in many respects. Table 2 illustrates this with some properties of the $Cr(C_2O_4)_2(H_2O)_2^-$ ion.

(b) Optical isomerism

Many potentially asymmetric tris- and tetraoxalato complexes have been fully or at least partially resolved. Conflicting evidence reported in certain cases is discussed along with the methods of resolution employed. In table 3 are listed oxalato complexes which have been

TABLE 2*

Optical and acid-base properties of $Cr(C_2O_4)_2(H_2O)_2^-$

$Cr(C_2O_4)_2(H_2O)_2^-$	$\lambda_{max.}$	ϵ	pK_1	pK_2
	$m\mu$			
trans (pink-red)	416	34.4	7.5	10.5
	555	32.0		
cis (blue-green)	416	68.5	7.5	9.7
	562	51.0	6.4†	8.8†

* Data from reference 98. † Data from reference 164.

TABLE 3

Asymmetric oxalato complexes

Complex		References
$Al(C_2O_4)_3^{3-}$	Resolved	(425)
	Unsuccessful	(212, 237a)
$Cr(C_2O_4)_3^{3-}$	Resolved	(204, 436)
$Fe(C_2O_4)_3^{3-}$	Resolved	(237a, 411)
	Unsuccessful	(212)
$Co(C_2O_4)_3^{3-}$	Resolved	(204)
$Ga(C_2O_4)_3^{3-}$	Unsuccessful	(127, 293)
	Resolved	(311)
$Rh(C_2O_4)_3^{3-}$	Resolved	(437)
$Ir(C_2O_4)_3^{3-}$	Resolved	(101, 102)
$Ge(C_2O_4)_3^{2-}$	Partially resolved	(294)
$[Coen_2C_2O_4]^+$	Resolved	(441)
$[Cren(C_2O_4)_2]^-$	Resolved	(66)
$[Co(NH_3)_2C_2O_4(NO_2)_2]^-$	Resolved	(412)
cis-$[Rh(C_2O_4)_2Cl]^{3-}$	Resolved	(105)
cis-$[Ir(C_2O_4)_2Cl_2]^{3-}$	Resolved	(104)
$[RuPy(C_2O_4)_2NO]^-$	Resolved	(77)
$Zr(C_2O_4)_4^{4-}$	Unsuccessful	(215)
$U(C_2O_4)_4^{4-}$	Resolved	(272)
	Unsuccessful	(214)

the subject of such resolution experiments.

The resolution of the anionic oxalato complexes is accomplished by standard techniques of fractional recrystallization, precipitation, or extraction, utilizing the cationic form of an easily separable optically active compound, for example, quinine, strychnine, cinchonine, or brucine. In certain cases an optically active complex ion like $Co(en)_3^{3+}$ has also been found useful as a precipitating agent. Strychnine has been successfully employed in the resolution of $Co(C_2O_4)_3^{3-}$, $Cr(C_2O_4)_3^{3-}$, $Rh(C_2O_4)_3^{3-}$, and $Ir(C_2O_4)_3^{3-}$ (204).

Several investigations on $Al(C_2O_4)_3^{3-}$ (212) and $Fe(C_2O_4)_3^{3-}$ (212, 237a) prove conclusively that the resolution of these complex ions is not possible by conventional methods.[1] This evidence of their labile ionic character is further corroborated by the practically instantaneous exchange of the ligand as shown by experiments using radioactive oxalate (265, 266). Conflicting reports in the case of $Al(C_2O_4)_3^{3-}$ may be due to the presence of an impurity or to some autocatalysis of a short-lived active intermediate formed during the resolution process. For $U(C_2O_4)_4^{4-}$, the alleged resolution into the *d*- and *l*-forms (271, 272) has been shown to be wrong, as the observed rotations were found to be largely due to traces of quinine iodide left in solution when quinine was used as a resolving agent (214).

An interesting example of the first recorded resolution of a hexacoördinated outer-orbital complex of a tetrapositive ion is that of $Ge(C_2O_4)_3^{2-}$ (294). Strychnine and quinine salts were used for the purpose and at least a partial resolution of the $Ge(C_2O_4)_3^{2-}$ ion was effected, suggesting predominantly covalent character for the complex ion. Exchange experiments with radioactive oxalate or radiogermanium should provide further information about the nature of the $Ge(C_2O_4)_3^{2-}$ ion.

Resolution of the $Ir(C_2O_4)_2Cl_2^{3-}$ ion (104) clearly establishes the cis configuration of this ion, as the trans form cannot exhibit optical activity by reasons of symmetry.

2. Spectroscopic data: ultraviolet, visible, and infrared

Metal oxalato complexes offer an interesting series of compounds for the spectrophotometric study of metal-oxygen (M—O) bonds. A number of general discussions of this approach have appeared in the literature (18, 112a, 148, 160, 161, 162, 277, 370). Specific data on their absorption spectra are presented in tables 4, 5, and 6. The absorption spectra in the visible and ultraviolet regions were in general run in water as solvent, and in some cases the solution contained excess added oxalate ion to stabilize the oxalato complex under observation. An interesting example is the work on $Cr(C_2O_4)_3^{3-}$. A comparison of the spectra in H_2O and D_2O showed nearly complete absence of crystal-field splitting (183), in contrast to $Cr(H_2O)_6^{3+}$, where the crystal-field splitting is significant. Although the absorption spectra of $Cr(C_2O_4)_3^{3-}$ and $Cr(H_2O)_6^{3+}$ resemble each other closely, this relatively small crystal-field effect in the case of $Cr(C_2O_4)_3^{3-}$ confirms the observation that the

TABLE 4

Visible absorption spectra of metal oxalato complexes

Oxalato Complex	$\lambda_{max.}$	ϵ_{molar}	References
	$m\mu$		
$Cu(C_2O_4)_2^{2-}$	700	33.5	(163)
$Cr(C_2O_4)_3^{3-}$ (0.01 *M*)	420	97	(9)
	570	75	
$Mn(C_2O_4)_3^{3-}$ (0.01 *M*) (oxalate buffer)	520	308	(74)
$Fe(C_2O_4)_3^{3-}$	650		(47)
$Co(C_2O_4)_3^{3-}$ (0.1 *M*)	420	220	(9)
	605	170	
$Rh(C_2O_4)_3^{3-}$	520	8	(217)
	398	290	
$Ir(C_2O_4)_3^{3-}$	360 (shoulder)	~1000	(217)
$U(C_2O_4)_4^{4-}$ (0.01 *M*)	439	18.5	(214)
	492	34.1	ϵ's vary with concentration of ion, oxalate ion, and added inert salts
	507	33.4	
	562	26.4	
	665	84.0	
$TiOC_2O_4^-$	410		(398)
	580		

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[1] A partial resolution of a 50 per cent methanol/water solution of $(NH_4)_3Fe(C_2O_4)_3$ was effected by Krebs, Diewald, Arlitt, and Wagner (237a), who employed a very rapid chromatographic separation technique at −35°C.

TABLE 5

Ultraviolet absorption spectra of metal oxalato complexes

Oxalato Complex	$\lambda_{max.}$	ϵ_{molar}	Reference
	mμ		
$HC_2O_4^-$	250	38	(160)
$(CH_3)_2C_2O_4$	246	51	(160)
$Be(C_2O_4)_2^{2-}$	258	40	(160)
$Mg(C_2O_4)_2^{2-}$	254	46	(160)
$Mn(C_2O_4)_3^{3-}$	<245	~300	(18)
$Fe(C_2O_4)_3^{3-}$	256	2512	(18)
$Co(C_2O_4)_3^{3-}$	230	—	(18)
$Ni(C_2O_4)_2^{2-}$	392	63	(18)
	343 (min.)	11	
$Cu(C_2O_4)_2^{2-}$	252	2400	(160)
$Zn(C_2O_4)_2^{2-}$	257	73	(160)
$Cd(C_2O_4)_2^{2-}$	255	57	(160)
$Hg(C_2O_4)_2^{2-}$	253	670	(160)
$Pd(C_2O_4)_2^{2-}$	380	105	(18)
$Pt(C_2O_4)_2^{2-}$	280	3802	(18)
$Sn(C_2O_4)_2^{2-}$	350–230	Structureless absorption	(18)
$Pb(C_2O_4)_2^{2-}$	~250	No maximum	(18)
$VO(C_2O_4)_2^{2-}$	330	209	(417)
$In(C_2O_4)_3^{3-}$	258	50	(160)
$Ir(C_2O_4)_3^{3-}$	290	4500	(217)
$Zr(C_2O_4)_4^{4-}$	266	52	(160)
$Hf(C_2O_4)_4^{4-}$	260–270	—	(214)
$Th(C_2O_4)_4^{4-}$	259	47	(214)
$U(C_2O_4)_4^{4-}$	260 (shoulder)	—	(214)

spectra of complexes where the inner-orbital ligands remain fixed are insensitive to even drastic changes in solvent environment (49).

The ultraviolet absorption spectra of dimethyl oxalate and many carboxylic acids and their esters have a characteristic band of low intensity in the region 210–260 mμ. This may be identified with the covalently bound carboxyl group and is most likely due to transitions of the π electrons of the >C=O group. The absence of this low-intensity band in the ultraviolet absorption spectrum of aqueous potassium oxalate solution and the existence of only an inflexion (see figure 3) in the case of aqueous oxalic acid solution indicate there are no covalently bound carboxyl groups as such in these compounds. Instead, only oxalate ion is present, in which all the oxygen atoms are equivalent. If, however, one examines the ultraviolet absorption spectrum of a dilute aqueous solution of oxalic acid (10^{-2} *M*) in 0.1 *M* or 1.0 *M* hydrochloric acid, it is found (160) that the spectrum approaches the shape of that of dimethyl oxalate and, in 93 per cent sulfuric acid, almost duplicates the latter but has lower absorbance. These observations are consistent with the complete suppression of the ionization of oxalic acid (p*K*'s 1.25 and 4.28) in strong mineral acids. Similar support is obtainable from a study of the infrared spectra of carboxylic acids, esters, and salts, indicating the different nature of carboxyl groups in these compounds. Study of the ultraviolet and infrared absorption spectra of the metal oxalato complexes, therefore, throws much light on the structural characteristics of coördinated oxalate and indicates whether it is "ionic" or "covalent" (326) in nature.

The ultraviolet absorption spectra of a great majority of the oxalato complexes (see table 5) resemble those of dimethyl oxalate and molecular oxalic acid, with a low intensity band in the region 250–270 mμ. The maxima seem to vary with the cation. Table 7 illustrates the interesting relation between the absorption maximum and the size and charge of the cation (160). The absorption maximum, $\lambda_{max.}$, is seen to increase smoothly

TABLE 6

Infrared absorption spectra of metal oxalato complexes

Oxalato Complex	Absorption Frequencies	Reference
$(CH_3)_2C_2O_4$	1770 1776	(370)
$Li_2C_2O_4$	1650 vs	(370)
$Na_2C_2O_4$	1640 vs	(370)
$K_2C_2O_4 \cdot H_2O$	1650 1628	(160)
	1600 vs	
$CaC_2O_4 \cdot H_2O$	1620 vs	(370)
$BaC_2O_4 \cdot H_2O$	1620 1600	(370)
$K_2Be(C_2O_4)_2 \cdot 2H_2O$	1728 1704	(160)
$K_2Mg(C_2O_4)_2 \cdot 2H_2O$	1653 b	(160)
$K_2Cd(C_2O_4)_2 \cdot 2H_2O$	1610 b	(160)
$K_2Cu(C_2O_4)_2 \cdot 2H_2O$	1673 1640 sh	(160)
$K_2Mn(C_2O_4)_2 \cdot 2H_2O$	1635 b	(160)
$K_2Ni(C_2O_4)_2 \cdot 6H_2O$	1635 b	(160)
$K_2Pd(C_2O_4)_2 \cdot 2H_2O$	1705 vs 1680 vs	(370)
$[Pd(NH_3)_2(C_2O_4)]$	1695 vs 1665 vs 1630 sh* (*NH_3 stretching)	(370)
$K_3Al(C_2O_4)_3 \cdot 3H_2O$	1725 vs 1695 vs 1400 vs	(370)
$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	1710 vs 1680 vs 1400 vs	(370)
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	1710 vs 1680 vs 1390 vs	(370)
$K_3Co(C_2O_4)_3 \cdot 3H_2O$	1710 vs 1680 vs 1397 vs	(370)
$K_3Sb(C_2O_4)_3 \cdot 3H_2O$	1715 sh 1650 b	(160)
$Na_2Cu(C_2O_4)_2(H_2O)_2$	1725 m 1680 vs 1412 vs	(370)
$Na[Cr(C_2O_4)_2(H_2O)_2] \cdot 5H_2O$	1715 vs 1690 vs 1660 vs 1395 vs	(370)
$K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$	1715 vs 1690 vs 1660 vs 1395 vs	(370)
$K_3[Rh(C_2O_4)_2Cl_2] \cdot H_2O$ (cis)	1700 s 1670 s, b 1654 s, b 1402 s	(85)
$K_4Zr(C_2O_4)_4 \cdot 5H_2O$	1667 1398	(214)
$K_4Hf(C_2O_4)_4 \cdot 5H_2O$	1669 1405	(214)
$K_4Th(C_2O_4)_4 \cdot 4H_2O$	1639 1424	(214)
$K_4U(C_2O_4)_4 \cdot 5H_2O$	1618 1422	(214)

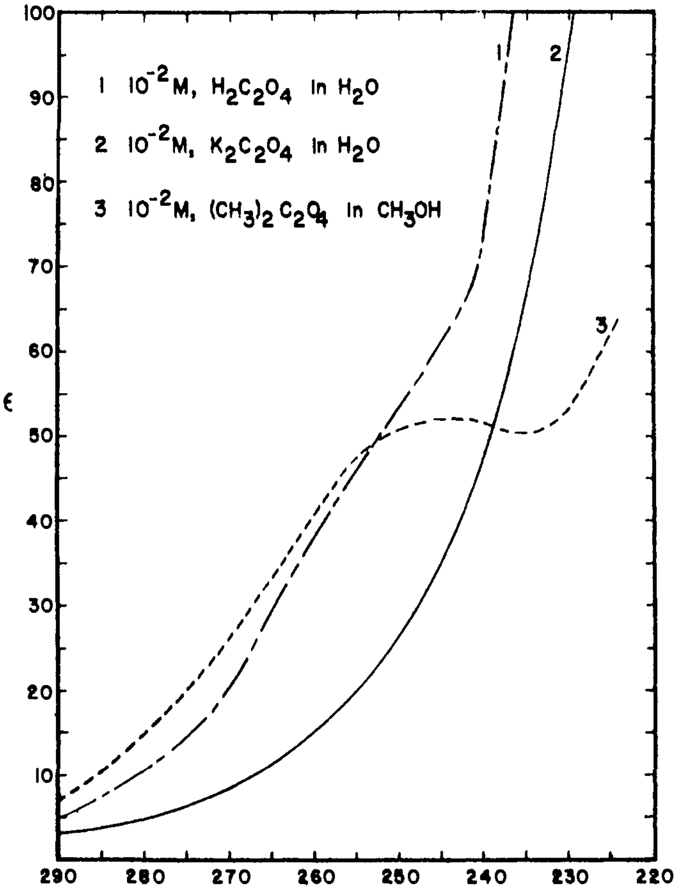


FIG. 3. Ultraviolet absorption spectra of ionically and covalently bound oxalate (from Graddon (160)). Reproduced by courtesy of Pergamon Press, Inc., New York City.

with z/d^2, where z is the oxidation number of the cation and d is the "ideal" covalent-bond distance from metal to oxygen (160). In other words, the low-intensity band, which is characteristic of a covalently bound oxalate, is displaced toward longer wavelengths as the coulombic force of attraction between the cation and the coördinated oxalate group increases. Graddon's theoretical treatment (160) of the electronic transition energy, E, associated with the wavelength of the absorption band is applicable here. The theory shows that the experimentally determined electronic transition energies are related to the properties of the coördinating cation by the equation:

$$E = -kz/l^2$$

where E is the electronic transition energy, k is a constant, z is the oxidation number of the cation, and l is the distance of the cation from the carbonyl group (see figure 4). The calculated and experimental values for k are 42 and 24, respectively. They are in remarkably good agreement considering the various approximations made at each stage in the treatment, which is based entirely on classical electrostatistics.

TABLE 7

*Ultraviolet absorption maximum and size of cation**

Oxalato Complex	$\lambda_{max.}$	z/d^2
I. Metal ion with inert gas configuration		
	mμ	
$Mg(C_2O_4)_2^{2-}$	254	0.44
$Be(C_2O_4)_2^{2-}$	258	0.62
$Th(C_2O_4)_4^{4-}$	259	0.67
$Al(C_2O_4)_3^{3-}$	260	0.70
$Zr(C_2O_4)_4^{4-}$	266	0.78
II. Metal ion with filled *d* shell		
$Hg(C_2O_4)_2^{2-}$	253	0.41
$Cd(C_2O_4)_2^{2-}$	255	0.41
$Zn(C_2O_4)_2^{2-}$	257	0.48
$In(C_2O_4)_2^{-}$	258	0.61
$Be(C_2O_4)_2^{2-}$	258	0.62

* Data from Graddon (160).

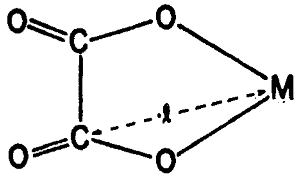


FIG. 4. Chelation of oxalate. ——, C—C—O angle 118°; O—M—O angle β°; C—C distance, 1.43 A.; C—O distance, 1.36 A.; M—O distance, d A. The values of the coördination angle, β, are 109.5°, 90°, and 70.5° for tetrahedral, octahedral, and eight coördination, respectively. The d is the sum of the "ideal" covalent radii of the atoms M and O. See Graddon (160).

The infrared absorption spectra of the simple and complex oxalates (see table 6) run by the Nujol mull or potassium bromide disk method check well in many cases. Table 6 shows only frequencies that are necessary for the purpose of comparison of the two types of binding, ionic and covalent, in the various metal oxalato complexes cited. A covalently bound oxalate group, as in dimethyl oxalate, gives rise to absorption in the region 1720–1750 cm.$^{-1}$ characteristic of >C═O stretching frequency and ionically bound oxalates (*cf.* simple oxalates) at 1600–1650 cm.$^{-1}$ The spectra of various oxalato complexes show a very strong absorption in the neighborhood of 1700 cm.$^{-1}$, indicating a certain degree of covalent character of the bound oxalate in the complex. It has been estimated, for example, that with the complexes of iron(III), aluminum(III), chromium(III), and cobalt(III), there is 50 per cent covalent character (370).

For simple oxalate monohydrates, $K_2C_2O_4 \cdot H_2O$, $CaC_2O_4 \cdot H_2O$, and $BaC_2O_4 \cdot H_2O$, the broad absorption band at 680 cm.$^{-1}$ has been identified with the water molecule, since the band disappeared on deuteration (370). Dehydration of the oxalato complexes of manganese, nickel, copper, and cadmium caused no significant change in the infrared absorption spectrum. Strong hydrogen bonding is indicated, however, in the case of the hydrated crystalline magnesium complex, $K_2Mg(C_2O_4)_2 \cdot 2H_2O$. The coördination of water molecules to magnesium is also supported by the impossibility of dehydrating the complex without decomposition, thus suggesting an octahedral structure for the anion $Mg(C_2O_4)_2(H_2O)_2^{2-}$ (160). In this connection, it is interesting to note that some recent dehydration (334) and proton magnetic resonance studies (177) of $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ indicate an intra-hydrogen-bonded ion, as shown in figure 5.

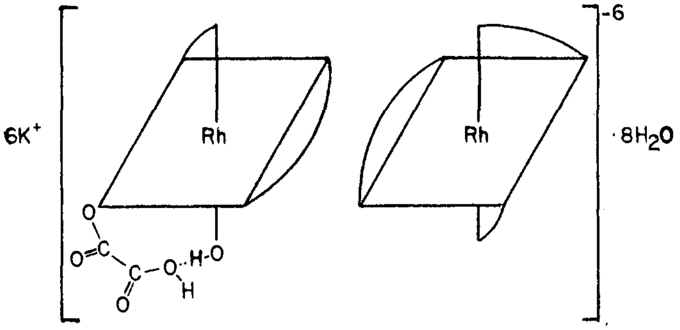


FIG. 5. Structure of $K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$ (Gutowsky, Porte, and Harris (177)).

Other studies (147) on infrared absorption characteristics have shown that it is possible to discriminate between coördinated water and crystal water. For example, *trans*-$KCr(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$ shows two bands at 1012 and 965 cm.$^{-1}$, whereas $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ does not, ruling out the existence of coördinated water in the latter. In aqueous solution, however, the results of isotopic exchange between $Cr(C_2O_4)_3^{3-}$ and $\overset{*}{C}_2O_4^{2-}$ (166) and other substitution reactions of the $Cr(C_2O_4)_3^{3-}$ ion are best interpreted in terms of a *monoaquated ion intermediate*, the existence of which has been supported by (*1*) studies of the proton relaxation phenomenon (298) and (*2*) application of the Gross–Butler equation to rates of aquation of $Cr(C_2O_4)_3^{3-}$ in H_2O–D_2O solvent mixtures (238) (see Section III,D,3,(a)).

3. Magnetic susceptibilities

The magnetic susceptibilities of oxalic acid and simple oxalates have been determined by several workers (275, 276, 343, 420). Both in the solid state and in solution, the ionic magnetic susceptibility, $\chi_{C_2O_4^{2-}}$, for the oxalate ion may be obtained from the data. Interest in such experimental determination of the magnetic susceptibilities in the case of oxalato complexes is centered on the metal ion and not on the oxalate ion as such. In table 8 are shown a number of observed and calculated magnetic moments and also the number of unpaired electrons in the central metal ion of the complex. Magnetic data offer convincing evidence for the bond type in these complexes; for example, both $Mn(C_2O_4)_3^{3-}$ and $Fe(C_2O_4)_3^{3-}$ are definitely ionic, as confirmed by other studies (see Section III,D,3,(c)).

TABLE 8

Magnetic moments of oxalato complexes

Oxalato Complex	Magnetic Moment (in Bohr magnetons)		Number of Unpaired Electrons	References
	$\mu_{obs.}$	$\mu_{calc.}$*		
$K_3Al(C_2O_4)_3 \cdot 3H_2O$	Diamagnetic		0	(212)
$H_4VO(C_2O_4)_3$(?)	1.4 (?)	1.73	1	(180, 455)
$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	3.75	3.88	3	(212)
$K_3Mn(C_2O_4)_3 \cdot 3H_2O$	4.88	4.90	4	(212)
$K_3[Mn(C_2O_4)_2(OH)_2] \cdot 2H_2O$	2.79 (?)	3.88	3	(168)
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	5.75	5.91	5	(212)
$K_2Co(C_2O_4)_2$	4.97	3.88	3	(139)
$K[Ru(C_2O_4)_2(NO)(C_5H_5N)]$	Diamagnetic		0	(53)
$K_3Co(C_2O_4)_3 \cdot 3H_2O$	Diamagnetic		0	(29, 212)
$K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$	Diamagnetic		0	(212)
$K_3Ir(C_2O_4)_3 \cdot 4.5H_2O$	Diamagnetic		0	(212)
$K_4[Re(C_2O_4)_2(OH)_2O]$	Diamagnetic		0	(209)
$K_4U(C_2O_4)_4 \cdot 5H_2O$	2.5 (±0.3)	2.83	2	(214)

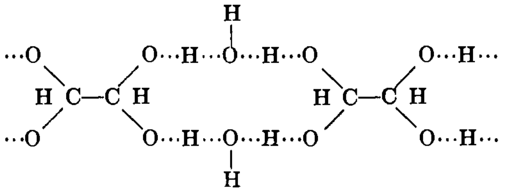
* Calculated on the "spin only" formula, $\mu = 2\sqrt{S(S+1)}$.

The high value of 4.97 for $\mu_{obs.}$ for $K_2Co(C_2O_4)_2$ places this compound among other cobalt(II) compounds which are generally classed as "ionic" complexes from the magnetic data alone (140, 318). No data on the magnetic susceptibilities of the compounds containing the $Co(C_2O_4)_3^{4-}$ ion are presently available. Such data would enable calculation of its magnetic moment and classification of it into the sp^3d^2 or d^2sp^3 grouping. The ion, however, is well characterized in solution (see table 11).

Although the value reported for $\mu_{obs.}$ in the case of $K_4U(C_2O_4)_4 \cdot 5H_2O$ is somewhat uncertain, there is no doubt that the compound is paramagnetic in solution and the observed moment corresponds to two unpaired electrons. It is likely that the two electrons, in excess of the inert radon configuration present in the uranium(IV) ion, are unpaired in this complex also. Further evidence in this direction is available from the studies on the acetylacetonates (197) and the benzoylacetonates (358) of uranium(IV).

4. Determination of crystal structure

Investigations on the crystal structure of different forms of oxalic acid [$H_2C_2O_4 \cdot 2H_2O$ (95, 122, 219, 335, 453), α-$(COOH)_2$ (90), β-$(COOH)_2$ (193)] and of simple oxalates [$(NH_4)_2C_2O_4 \cdot H_2O$ (194, 207), $K_2C_2O_4 \cdot H_2O$ (193), $Rb_2C_2O_4 \cdot H_2O$ (193), $Na_2C_2O_4$ (208), and $Ag_2C_2O_4$ (169)] have clearly shown the characteristic difference between the oxalate ion and the oxalic acid molecule. For oxalic acid dihydrate the data conclusively show a chain structure via hydrogen bonding, as shown below.



The O···H···O distance of 2.52 A. is the shortest known hydrogen bond (122). Further evidence from the dihydrates of acetylenedicarboxylic acid (123) and diacetylenedicarboxylic acid (124), which exhibit the same pattern, confirms the chain structure. Also a recent study of the nuclear magnetic resonance spectrum of $(COOH)_2 \cdot 2H_2O$ suggests that oxalic acid dihydrate does not contain the H_3O^+ ion (347). Another example having a chain structure resembling that of β-$(COOH)_2$ is silver oxalate (169). On the other hand, sodium oxalate (208) is a unique oxalate with no water of crystallization. It allows the study of the structure of the oxalate ion in a normal ionic environment, unlike the simple oxalate hydrates of other elements. Work on sodium oxalate shows that the oxalate ion is planar. The interatomic distances and the bond angles are illustrated in figure 6. The angles C—C—O_I and C—C—O_{II} were at first reported unequal (208), but this is now ascribed to possible error of the x-ray analysis. It is therefore concluded that the free oxalate ion has V_h symmetry and that the bound oxalate has C_{2v} symmetry (148). This conclusion is further substantiated by the x-ray data of *trans*-$K[Cr(C_2O_4)_2(H_2O)_2] \cdot 3H_2O$ (313), for which various interatomic distances and bond angles are shown in figure 7.

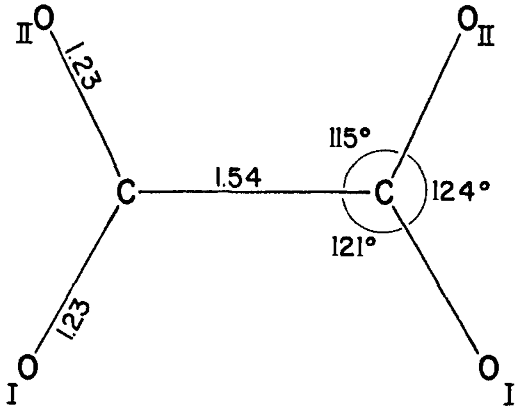


FIG. 6. Structure of the oxalate ion (Jeffrey and Parry (208)).

Available crystallographic data of several other oxalato complexes are presented in table 9. It must be pointed out that only a few have been investigated thoroughly. Incomplete x-ray data are not sufficient

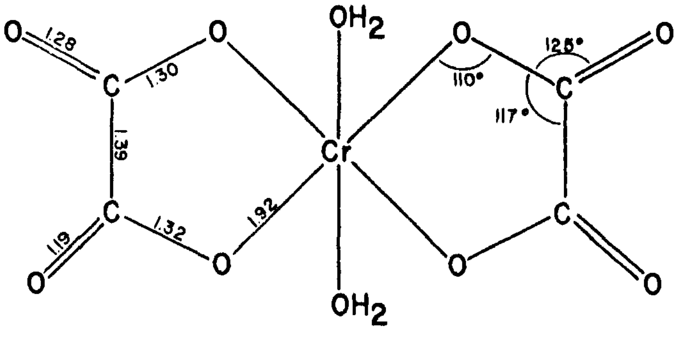


FIG. 7. Structure of the *trans*-$Cr(C_2O_4)_2(H_2O)_2^-$ ion (Van Niekerk and Schoening (313)).

TABLE 9

Crystallographic data on oxalato complexes

Compound	Symmetry Classification	Space Group	*a*	*b*	*c*	*β*			Reference
			A.	*A.*	*A.*				
$K_3Al(C_2O_4)_3 \cdot 2.5H_2O$	Monoclinic								(448)
$K_3Cr(C_2O_4)_3 \cdot 3H_2O$	Monoclinic	$P(2_1)/c\text{–}C_{2h}^5$	7.71	19.74	10.40	108°0′			(314)
$Rb_3Cr(C_2O_4)_3 \cdot xH_2O$	Monoclinic	$P(2_1)/c$	7.81	19.60	10.40	108°0′			(315)
$(NH_4)_3Cr(C_2O_4)_3 \cdot 2H_2O$	Triclinic	$P\bar{1}$	7.79	10.90	10.73	98°10′ (*α*) 112°36′ (*β*) 67°22′ (*γ*)			(316)
trans-$KCr(C_2O_4)_2(H_2O)_2 \cdot 3H_2O$	Monoclinic	$P(2/c)\text{–}C_{2h}^4$	7.85	5.72	13.88	109°30′			(313)
$Na_3Cr(C_2O_4)_3 \cdot 4.5H_2O$	Monoclinic								(448)
$K_3Mn(C_2O_4)_3 \cdot 3H_2O$	Monoclinic		*a*:*b*:*c*						(223)
$K_3Fe(C_2O_4)_3 \cdot 3H_2O$	Monoclinic		0.9923:1:0.3925			85°40′			(203)
$K_3Co(C_2O_4)_3 \cdot 3.5H_2O$	Triclinic		0.5963:1:0.6590			91°42′ (*α*) 101°23′ (*β*) 88°22′ (*γ*)			(203)
$(NH_4)_3Co(C_2O_4)_3 \cdot 3H_2O$	Monoclinic								(87)
$K_3Sb(C_2O_4)_3 \cdot 3H_2O$	Orthorhombic								(342)
$[Pd(NH_3)_2C_2O_4]$	Monoclinic	$P(2_1)/m$	8.1	10.47	3.67	122°23′			(270)
$K_4Zr(C_2O_4)_4 \cdot 5H_2O$	Monoclinic	$P(2_1)/a$	16.10	12.34	10.23	(94°)			(214)
$K_4Hf(C_2O_4)_4 \cdot 5H_2O$	Monoclinic	$P(2_1)/a$	15.94	12.35	10.62	94°20′			(214)
$K_4Th(C_2O_4)_4 \cdot 4H_2O$	Monoclinic								(214)
$K_4U(C_2O_4)_4 \cdot 5H_2O$	Monoclinic								(214)
			a:*b*:*c*			*α*	*β*	*γ*	
$K_3Rh(C_2O_4)_3 \cdot 4.5H_2O$	Triclinic		1.0732:1:1.0316			98°11′	104°17′	66°12′	(203)
						92°45′	102°4′	67°24′	(203)
$K_3Ir(C_2O_4)_3 \cdot 4.5H_2O$	Triclinic		1.0771:1:1.0405			98°38′	104°3′	66°9′	(203)
			0.732 :1:1.956			88°35′	94°30′	57°1′	(454)
$K_2OsO_2(C_2O_4)_2 \cdot 2H_2O$	Triclinic		0.500 :1:1.055			93°29′	91°7′	99°28′	(117)
			a:*c*			*α*			
$K_3Co(C_2O_4)_3 \cdot H_2O$	Trigonal		1:0.8968			100°27′			(203)
$K_3Rh(C_2O_4)_3 \cdot H_2O$	Trigonal		1:0.8938			100°38′			(203)
$K_3Ir(C_2O_4)_3 \cdot H_2O$	Trigonal		1:0.9520			100°28′			(203)

$K_2Pb(C_2O_4)_2$ is reported to contain planar lead groupings: *a* = 4.03; *b* = 3.99; *c* = 4.85 (91).

for determination of structure and should be treated with caution. Evidence comes from x-ray studies on the tetraoxalato complexes of zirconium(IV) and hafnium(IV) for two kinds of complex ions, each being the mirror image of the other. This probably indicates that the complex ions are optically active, although further proof would be desirable (214).

5. *Miscellaneous data*

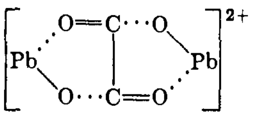
Among several other methods that offer some insight into the structure of oxalato complexes is the one based on the determination of the *dialysis coefficients.* Ionic formulas were suggested by such studies (58) in aqueous solution for the following metal oxalato complexes:

$Fe_2(C_2O_4)_4^{4-}$
$Co_2(C_2O_4)_4^{4-}$
$Ni_2(C_2O_4)_4^{4-}$
$Mn_2(C_2O_4)_4^{4-}$
$Cu_2(C_2O_4)_4^{4-}$
$Cd_2(C_2O_4)_4^{4-}$
$Zn_2(C_2O_4)_4^{4-}$
$TiO(C_2O_4)_2^{2-}$
$VO(C_2O_4)^{2-}$
$UO_2(C_2O_4)^{2-}$
$Fe(C_2O_4)_3^{3-}$
$Co(C_2O_4)_3^{3-}$
$Mn(C_2O_4)_3^{3-}$
$Cr(C_2O_4)_3^{3-}$
$Th_2(C_2O_4)_8^{8-}$
$Zr_2(C_2O_4)_{16}^{16-}$

At least some of the experimentally found ionic weights agreed remarkably well with the ones calculated from the proposed formulas, considering the limitations of the dialysis method (206, 277). The formula of the thorium complex is confirmed in a recent study using a cellophane membrane (145).

The *ion-exchange method* has proved valuable in many cases (see Section III,C,2), particularly in studying the structure of certain basic chromium oxalato complexes (176a) and also that of the unusual copper complex $Cu(HC_2O_4)_6^{4-}$ (82).

An interesting series of compounds containing the $Pb_2C_2O_4^{2+}$ ion



in which all four oxygen atoms are bonded to metal has been reported (430) on the basis of solubility studies. Similar ions containing zinc and cadmium (423) are postulated to explain the increased solubility of zinc oxalate and cadmium oxalate in the presence of excess cation.

C. STABILITY AND STABILITY CONSTANTS

Several methods for the detection of the presence of complex ions and the determination of their stability constants are described in standard textbooks on coordination chemistry (27, 48, 256, 274). In this section, the methods that have been successfully employed in the study of the oxalato complexes will be discussed exclusively. Available data on the stability constant are presented in table 11. Only the cumulative stability constants are listed in the table. It is noted that in many cases there is good agreement in the values for the stability constant determined by more than one procedure. Some of the data relating to the stepwise stability constants are discussed under "Methods of Determination" below.

1. *Methods of determination*

(a) Spectrophotometric method

Job's method of continuous variation (107, 210, 216, 274, 312) has been the most frequently used for the spectrophotometric determination of the composition and stability of complex ions both in the visible and in the ultraviolet region. The single-step instability constants recently reported from such studies for the three aluminum oxalato complexes $AlC_2O_4^+$, $Al(C_2O_4)_2^-$, and $Al(C_2O_4)_3^{3-}$ are 5.5×10^{-8}, 1.4×10^{-5}, and 4.9×10^{-2}, respectively (24).

Studies on the ultraviolet absorption spectra of the $SnCl_4$–$K_2C_2O_4$ system suggest the complexes $Sn(C_2O_4)_2^0$ and $Sn(C_2O_4)_4^{4-}$ (108); this is in keeping with the previous observations made in conductometric studies (110).

The reaction

$$VO^{2+} + 2C_2O_4^{2-} = VO(C_2O_4)_2^{2-}$$

has been followed spectrophotometrically at 300 mμ, and a 1:2 complex was reported (417). At pH 2–3 and ionic strength 0.5 the pK for $VO(C_2O_4)_2^{2-}$ is 9.76. At pH > 3 precipitation apparently occurs. In an independent study on the same system (456), a combination of potentiometric pH measurements, conductance measurements, and optical density data at 572–574 mμ and 726 mμ shows the formation of a blue complex, $VO(HC_2O_4)_2^0$, stable at pH 1.4–4.5. Although the presence of the ion $VO(HC_2O_4)^+$ is suggested, no evidence is available for $[VO(OH)C_2O_4]^-$.

Studies on the oxalato complexes of molybdenum(IV), molybdenum(V), and molybdenum(VI) indicate the presence of the ions $(MoOC_2O_4)^0$ (392), $(MoO_2C_2O_4)^-$ (32, 391), and $(MoO_3C_2O_4)^{2-}$ (305, 350, 362, 393), respectively. Preparation of a molybdenum(IV) complex in the solid form has been recently achieved by electrolytic reduction of ammonium molybdate in the presence of oxalic acid to give a yellow-brown solid having the composition $(NH_4)_4Mo(C_2O_4)_4 \cdot 8H_2O$ (395). Spectrophotometric investigation of the process

$$MoO_4^{2-} + C_2O_4^{2-} + 2H^+ = MoO_3C_2O_4^{2-} + H_2O$$

at 260–300 mμ confirms a 1:1 complex, and the equilibrium constant reported for the reaction is 10^{13} (410).

The behavior of otherwise noncomplexing NpO_2^+ ion in the presence of the $C_2O_4^{2-}$ ion is indeed interesting. A detailed study of the neptunium(V)–oxalate system showed that the peak at 983 mμ in the NpO_2^+ spectrum is shifted to 990 mμ, presumably owing to complexation in aqueous solution. The association constants, K_1 and K_2, for the mono- and dioxalato species are 2.00×10^3 and 6.10×10^3, respectively, at pH 4.87 and ionic strength 0.5 (175).

$$K_1 = (NpO_2C_2O_4^-)/(NpO_2^+)(C_2O_4^{2-})$$

$$K_2 = [NpO_2(C_2O_4)_2^{3-}]/(NpO_2C_2O_4^-)(C_2O_4^{2-})$$

(b) Solubility method

Since a great majority of the metals form sparingly soluble simple oxalates, as well as complex oxalates, increase in the solubility of a simple oxalate in excess oxalate forms the basis of this method. For example, the solubility of lead oxalate increases linearly with excess oxalate-ion concentration (231), indicating the formation of $Pb(C_2O_4)_2^{2-}$ (see table 11). Solubilities have also been useful in obtaining the stability constants of oxalate complexes of magnesium(II), nickel(II), cadmium(II), and cobalt(II) (34), and demonstrating complex formation in the case of copper(II), zinc(II), and thorium(IV) (59, 60, 60a).

The introduction of the radioisotope technique has enabled determination of solubilities at very low concentrations, and the technique has been used to obtain the solubility-product constants of the simple oxalates as well as the stability constants of the oxalato complexes of yttrium(III) (137), cerium(III) (94), and ytterbium(III) (93). The experimental procedure is to prepare equilibrium solutions by adding the radioactive rare earth ion to buffered oxalate solutions at constant temperature (25°C.) and to analyze for the hydrogen-ion activity by a pH determination, the total oxalate by permanganate titration, and the total rare earth content by radioassay. Experimental solubilities as well as calculated total rare earth concentrations are plotted as a function of oxalate-ion activity, as shown in figure 8 for yttrium. The curve is calculated from the relation:

$$Y_{total} = \frac{K_{sp}^{1/2}}{a_{C_2O_4^{2-}}^{3/2}} \frac{1}{\gamma_{Y^{3+}}} + \frac{a_{C_2O_4^{2-}}}{K_1\gamma_{YC_2O_4^+}} + \frac{a_{C_2O_4^{2-}}^2}{K_2\gamma_{Y(C_2O_4)_2^-}} + \frac{a_{C_2O_4^{2-}}^3}{K_3\gamma_{Y(C_2O_4)_3^{3-}}}$$

where $K_{sp} = (Y^{3+})^2(C_2O_4^{2-})^3$

$$K_1 = (Y^{3+})(C_2O_4^{2-})/(YC_2O_4^+)$$

$$K_2 = (Y^{3+})(C_2O_4^{2-})^2/[Y(C_2O_4)_2^-]$$

$$K_3 = (Y^{3+})(C_2O_4^{2-})^3/[Y(C_2O_4)_3^{3-}]$$

and γ's are the various activity coefficients (taken as unity). The $-\log (Y)_{total}$ vs. $-\log a_{C_2O_4^{-2}}$ curve resembles those obtained for cerium(III), neodymium(III), and ytterbium(III). A significant feature is that yttrium(III) forms a trisoxalato complex, as also does cerium(III), but not neodymium(III) and ytterbium(III). This may be explained as due to the relatively smaller size of the Y^{3+} ion as compared to the rare earth ions.

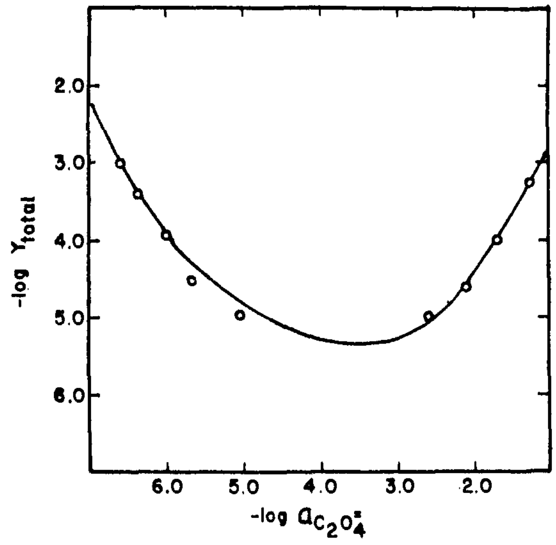


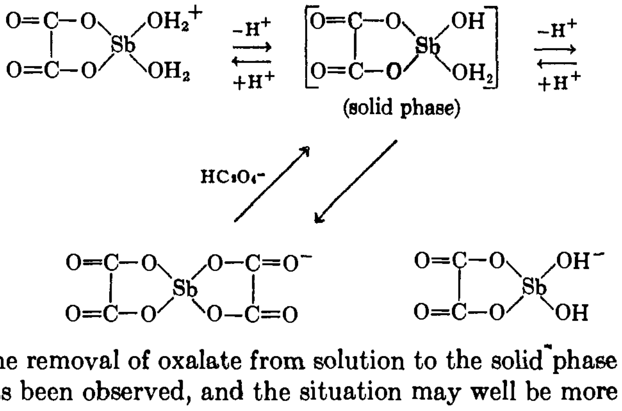
Fig. 8. Total yttrium concentration in buffered oxalate solutions (Feibush, Rowley, and Gordon (137)).

Studies of the solubility of antimony(III) oxide in solutions containing oxalate-bioxalate indicate an oxalato complex of antimony(III) (308):

$$SbO^+ + 2HC_2O_4^- = Sb(C_2O_4)_2^- + H_2O$$

$$K = 6.23 \times 10^6 \ (25°C.)$$

From the experimental K values at 25°, 27°, and 30°C., $\Delta F°$, $\Delta H°$, and $\Delta S°$ are calculated as 17 kcal. mole^{-1}, 60 kcal. mole^{-1}, and 142 e.u., respectively. The high positive value for $\Delta S°$ is attributed to chelation and the coördination number for antimony(III) in $Sb(C_2O_4)_2^-$ is reported as 4. Since the 4*d* and 5*s* levels are filled in antimony(III), it is surmised that the three 5*p* orbitals and one 5*d* orbital are involved in bond formation of the p^3d type (*cf.* tellurium(IV) chloride), resulting in weak bonds. This can be seen in the strong tendency of antimony(III) complexes to hydrolyze to antimony(III) oxide, where the coördination number for antimony(III) is 3. The following equilibria are also reported in the Sb_2O_3–oxalate system (309, 310):



The removal of oxalate from solution to the solid phase has been observed, and the situation may well be more complicated than the scheme presented indicates.

The solubility of uranyl oxalate in excess oxalate suggests the complex ion $UO_2(C_2O_4)_2^{2-}$ (79, 301) and in excess UO_2^{2+} the neutral complex $(UO_2C_2O_4)^0$ (331).

Recent studies on the solubility of uranium(IV) oxalate (170, 171) give evidence for the equilibria:

$$U(C_2O_4)_2(H_2O)_n \rightleftarrows U(C_2O_4)_2(H_2O)_{n-1}OH^- + H^+$$

$$U(C_2O_4)_2(H_2O)_n \rightleftarrows U(C_2O_4)(H_2O)_n{}^{2+} + C_2O_4{}^{2-}$$

The latter equilibrium is reported to contribute ~30 per cent to the overall process. It is also concluded that the ion $U(C_2O_4)_4{}^{4-}$ is a stronger acid than $Th(C_2O_4)_4{}^{4-}$.

(c) Kinetic method

An ingenious application of reaction rates to the estimation of stability constants of $MnC_2O_4{}^+$, $Mn(C_2O_4)_2{}^-$, and $Mn(C_2O_4)_3{}^{3-}$ has been reported as a result of the rate studies: (*1*) catalytic oxidation of oxalic acid by chlorine in the presence of manganese(III) (406); (*2*) catalytic oxidation of oxalic acid by bromine in the presence of manganese(III) (407); and (*3*) rate of disappearance of manganese(III) in the permanganate-oxalate reaction (408). It was assumed that the following rapid equilibria were maintained between Mn^{3+} and $C_2O_4{}^{2-}$, and that the oxidation of oxalate ion by manganese(III) proceeded by three independent first-order paths:

$$Mn^{3+} + C_2O_4{}^{2-} \rightleftarrows MnC_2O_4{}^+ \qquad K_1$$

$$MnC_2O_4{}^+ + C_2O_4{}^{2-} \rightleftarrows Mn(C_2O_4)_2{}^- \qquad K_2$$

$$Mn(C_2O_4)_2{}^- + C_2O_4{}^{2-} \rightleftarrows Mn(C_2O_4)_3{}^{3-} \qquad K_3$$

$$MnC_2O_4{}^+ \rightarrow \qquad k_1$$

$$Mn(C_2O_4)_2{}^- \rightarrow \qquad k_2$$

$$Mn(C_2O_4)_3{}^{3-} \rightarrow \qquad k_3$$

A detailed study, therefore, of the dependence on oxalic acid over a wide range gives sufficient data to estimate the values of the various constants. The following are the stepwise stability constants of the oxalate complex estimated in this work at 25.2°C. and ionic strength 2.0:

$$K_1 = 9.5 \times 10^9$$

$$K_2 = 3.9 \times 10^6$$

$$K_3 = 7.1 \times 10^2$$

The large decrease in going from K_1 to K_2 to K_3 in the oxalato complexes of manganese(III) is also observed with aluminum(III), gallium(III), chromium(III), and iron(III).

It is interesting to note that the equilibrium constant for the reaction

$$Mn(C_2O_4)_3{}^{3-} \rightleftarrows Mn(C_2O_4)_2{}^- + C_2O_4{}^{2-}$$

estimated as 1.4 × 10^{-3} (25.2°C., ionic strength 2) by the kinetic method, agrees reasonably well with the value 3.8 × 10^{-3} (0°C., lower ionic strength) reported earlier in a spectrophotometric study (74).

The analogous reaction

$$Cr(C_2O_4)_3{}^{3-} \rightleftarrows Cr(C_2O_4)_2{}^- + C_2O_4{}^{2-}$$

was involved in an isotopic exchange study, and from the kinetic data the equilibrium constant has been estimated as 3.5 × 10^{-4} at 75°C. (238). The only comparable figure in the literature was obtained from pH studies and is 3.4 × 10^{-6} at 32°C. (126). The two values are consistent if ΔH of the reaction has the reasonable magnitude of 20 kcal. mole^{-1}.

(d) Ion-exchange method

The ion-exchange method (373–375, 377) (in certain cases in conjunction with radioisotopes) has been useful in identifying oxalato complexes and in determining their stability constants. Studies of manganese(II) (257), cobalt(II) (142, 257, 376), copper(II) (82), zinc(II) (235, 376), cadmium(II) (235), germanium(IV) (133), zirconium(IV), hafnium(IV) (131), and uranium(IV) (257) merit mention.

Using Amberlite IRA-401 in the oxalate form, the solution containing the copper(II) complex was equilibrated at 30°C. for 18 hr. before analyzing for copper content, total oxalate, and hydrogen ion. Several experiments conducted in this way gave evidence for a hexacoördinated copper(II) complex of the formula $Cu(HC_2O_4)_6{}^{4-}$, stable on the resin phase, and in solution the well-known complex $Cu(C_2O_4)_2{}^{2-}$ (82).

Studies of the germanium(IV)-oxalate system indicate that the composition of the species depends largely on the pH of the solution. Below pH 3 the principal species is $Ge(C_2O_4)_3{}^{2-}$ and at pH 3-6, $GeO(C_2O_4)_2{}^{2-}$ and $GeO_2(C_2O_4)^{2-}$. At pH > 7 there was no evidence of any sorption of complexes on the resin (133).

By a combination of ion-exchange method using Dowex-50 and the various radioisotopes Mn^{54}, Co^{60}, Zn^{65}, Cd^{115}, Zr^{95}, Hf^{181}, and U^{223}, the stability constants of the respective oxalato complexes have been determined. These values seem to be in good agreement with those obtained by other methods (see table 11). Similar studies using Fe^{59} and Co^{60} indicate that the iron(II) oxalato complexes are more stable than the cobalt(II) oxalato complexes (128). Evidence for a pentaoxalato complex $M(C_2O_4)_5{}^{6-}$ of zirconium(IV) and hafnium(IV) is indicated (131). The following equilibrium constants were obtained for the equilibria in the $UO_2{}^{2+}$-oxalate system:

$$(UO_2HC_2O_4{}^+)/(UO^{2+})(HC_2O_4{}^-) = 2510$$

$$[UO_2(HC_2O_4)_2]/(UO_2HC_2O_4{}^+)(HC_2O_4{}^-) = 360$$

at 25°C., pH 0.90, and ionic strength 0.16. Somewhat lower values for the same equilibrium constants at 25°C. in 1 *M* perchloric acid and in 2 *M* perchloric acid are ascribed to the ionic strength effect (257).

Stability constants of the type

$$K = (MnX)/(Mn^{2+})(X^{2-})$$

where X^{2-} is oxalate, malonate, succinate, glutarate, pimelate, or azelate, were obtained by the ion-exchange method and showed interesting dependence on size of the chelate ring, as illustrated in figure 9. The greater stability in the case of five- and six-membered rings may well be due to an entropy effect (274).

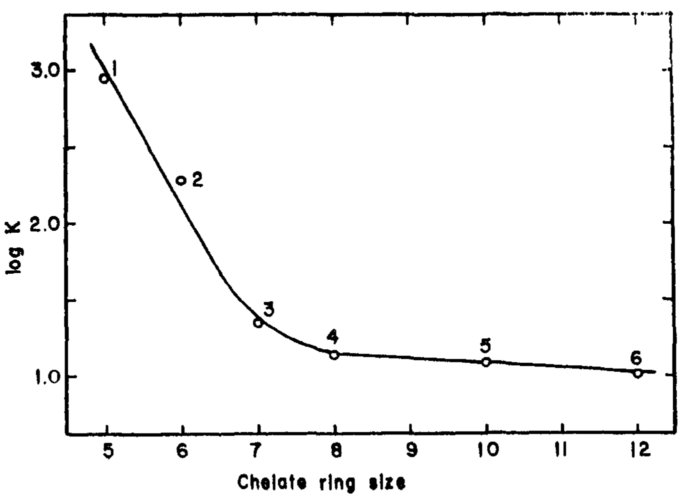


FIG. 9. Stability versus chelate ring size in manganese(II) dicarboxylates: (1) oxalate, (2) malonate, (3) succinate, (4) glutarate, (5) pimelate, (6) azelate (from Li, Westfall, Lindenbaum, White, and Schubert (257)). Reproduced by courtesy of the American Chemical Society.

An interesting example is the study of the oxalato complexes of plutonium(III), plutonium(IV), and plutonium(VI) by a combination of spectrophotometric (151), solubility (97, 150, 152, 154, 299, 319), ion-exchange (132, 153), potentiometric (299), and polarographic (144, 345, 426) methods.

Ion-exchange studies using KU-2 cation exchanger have shown that americium(III) forms oxalato complexes of the type $Am(C_2O_4)_2^-$, $Am(HC_2O_4)_3^0$, and $Am(HC_2O_4)_4^-$, and that their dissociation constants are 1-2 × 10^{-10}, 2.3 × 10^{-10}, and 1.0 × 10^{-11}, respectively (300).

(e) Solvent-extraction method

The solvent-extraction method in conjunction with radioisotopic tracers has been widely applied to the study of complex-ion equilibria (86, 100, 114, 201, 356, 357). Chloroform containing cupferron has been employed in the study of cobalt(II) oxalato complexes using Co^{60} as the tracer (376). With zinc(II), Zn^{65} was the tracer for extraction into chloroform containing 8-hydroxyquinoline (376). Stepwise stability constants for this ion determined by the solvent-extraction method are compared with those obtained from the ion-exchange method in table 10 at 25°C. and ionic strength 0.16.

(f) Potentiometric method

The essential details of the potentiometric method and its accuracy and reliability for the determination of the stability constants of complex compounds are well known (5, 48, 67, 69, 344). It has been applied with remarkable success in the study of the trisoxalato complexes of aluminum(III), chromium(III), iron(III), and gallium(III) (126). Experimentally, this involves measurement of the pH of equilibrium mixtures of known quantities of the trisoxalato complex with varying quantities of standard acid at constant temperature and ionic strength. From a knowledge of the K_1 and K_2 of oxalic acid under the same conditions, and by the application of Bjerrum's method, the following K_3 values are reported (126):

TABLE 10

Stability constants from solvent-extraction and ion-exchange methods (377)

Equilibrium	Solvent Extraction log *K*	Ion Exchange log *K*
$(ZnHC_2O_4^+)/(Zn^{2+})(HC_2O_4^-)$	—	1.72
$[Zn(HC_2O_4)_2]/(ZnHC_2O_4^+)(HC_2O_4^-)$	—	1.40
$(ZnC_2O_4)/(Zn^{2+})(C_2O_4^{2-})$	3.85	3.88
$[Zn(C_2O_4)_2^{2-}]/(ZnC_2O_4)(C_2O_4^{2-})$	2.35	2.52

	K_3
Chromium(III)	3.36 × 10^{-6}
Iron(III)	1.71 × 10^{-5}
Gallium(III)	2.85 × 10^{-3}
Aluminum(III)	2.08 × 10^{-4}

$K_3 = [M(C_2O_4)_2^-](C_2O_4^{2-})/[M(C_2O_4)_3^{3-}]$

Decomposition by acid of these trisoxalato complexes does not go beyond the bisoxalato stage even in the presence of much acid—in the case of chromium(III), as high as ~1 *M* (238). Apparently the bisoxalato complexes are very stable once they are formed (126). This conclusion is confirmed by recent kinetic studies of the acid-catalyzed aquation of the $Cr(C_2O_4)_2en^-$ ion, where the only observed reaction is substitution of water for ethylenediamine (368). The decomposition of $Al(C_2O_4)_2^-$ to $AlC_2O_4^+$ is indicated (126), although an earlier study (244) failed to detect the same. But evidence for $Al(C_2O_4)_2^-$ comes from many other sources—conductance, spectrophotometric, and thermometric studies (364)—and a value of 10^{-6} has been estimated for the equilibrium constant (126):

$$K = (Al^{3+})(C_2O_4^{2-})^2/[Al(C_2O_4)_2^-]$$

By a combination of conductance, potentiometric, and spectrophotometric studies of the gallium(III)-oxalate system it was shown that the complex ions $Ga_2(C_2O_4)_3^0$, $Ga(C_2O_4)_2^-$, and $Ga(C_2O_4)_3^{3-}$ occur in solution at pH 1.6–7.4 (365).

pH titrations have enabled evaluation of the following stepwise equilibrium constants (427): K_1 =

$10^{4.10\pm0.10}$, $K_2 = 10^{3.05\pm0.10}$, and $K_3 = 10^{1.36\pm0.10}$, where

$$K_1 = (NiC_2O_4)/(Ni^{2+})(C_2O_4^{2-})$$

$$K_2 = [Ni(C_2O_4)_2^{2-}]/(NiC_2O_4)(C_2O_4^{2-})$$

$$K_3 = [Ni(C_2O_4)_3^{4-}]/[Ni(C_2O_4)_2^{2-}](C_2O_4^{2-})$$

From similar pH measurements, three agreeing log K values are reported for the equilibrium

$$Mg^{2+} + C_2O_4^{2-} = MgC_2O_4^0$$

These are 2.55 (68), 2.65 (338), and 2.76 (20°C.) (387) at ionic strengths 0.2, 0.07, and 0.10, respectively.

Studies of the thorium(IV)–oxalate system indicate $Th(C_2O_4)^{4-}$ with a high order of stability (see table 11).

TABLE 11

Stability constants of oxalato complexes

Oxalato Complex	Log K	Temperature	Conditions μ	Method	References
		°C.			
$Al(C_2O_4)^+$	7.25	—	—	Spectrophotometric	(24)
$Mn(C_2O_4)^+$	9.98	25	2 M $HClO_4$	Kinetic	(407)
$Fe(C_2O_4)^+$	9.4	—	—	Potentiometric	(247)
$Y(C_2O_4)^+$	6.52	25	→0	Solubility	(137)
$Ce(C_2O_4)^+$	6.52	25	→0	Solubility	(94)
	6.04	—	2	Solubility	(23)
$Nd(C_2O_4)^+$	7.21	25	→0	Solubility	(94)
$Yb(C_2O_4)^+$	7.30	25	→0	Solubility	(93, 94)
$Ag(C_2O_4)^-$	~0	18	0.001	Electrical conductance	(371)
	2.41	25	1 M $LiClO_4$	Potentiometric	(83)
$Tl(C_2O_4)^-$	2.03	25	0.2	Potentiometric	(1)
	1.96	18	—	Potentiometric	(113)
$TiO(C_2O_4)^-$	2.65	23	—	Spectrophotometric	(398)
$MoO_3(C_2O_4)^{2-}$	13.0	—	—	Spectrophotometric	(410)
$Al(C_2O_4)_2^-$	13.0	—	→0	Potentiometric	(244, 255)
	6.0	32	0.01	Potentiometric	(126)
$Mn(C_2O_4)_2^-$	16.57	25	2 M $HClO_4$	Kinetic	(407)
$Fe(C_2O_4)_2^-$	16.2	—	→0	Potentiometric	(247)
$Y(C_2O_4)_2^-$	10.10	25	→0	Solubility	(137)
$Sb(C_2O_4)_2^-$	6.79	25	→0	Solubility	(309)
$Ce(C_2O_4)_2^-$	10.48	25	→0	Solubility	(94)
$Nd(C_2O_4)_2^-$	11.51	25	→0	Solubility	(94)
$Yb(C_2O_4)_2^-$	11.89	25	→0	Solubility	(93, 94)
$Be(C_2O_4)_2^{2-}$	~6–7	—	—	—	(50)
$Mg(C_2O_4)_2^{2-}$	4.38	25	→0	Solubility	(30)
$Mn(C_2O_4)_2^{2-}$	5.25	25	→0	Solubility	(296)
$Fe(C_2O_4)_2^{2-}$	9.57	—	—	Polarographic	(416)
	4.52	25	0.5 M $NaClO_4$	Solubility	(366)
	4.5	—	—	Polarographic	(366)
$Co(C_2O_4)_2^{2-}$	6.7	25	0.002	Solubility	(34)
	6.66	—	—	Ion exchange	(142)
$Ni(C_2O_4)_2^{2-}$	6.51	25	0.002	Solubility	(34)
	12.30	—	—	Polarographic	(363)
$Cu(C_2O_4)_2^{2-}$	8.3	18	0.01 M $Na_2C_2O_4$	Potentiometric	(59)
	10.32	~20	—	Polarographic	(286)
	7.48	—	—	—	(348, 349)
$Zn(C_2O_4)_2^{2-}$	7.36	25	→0	Solubility	(423)
	7.04	25	→0	Solubility	(81)
	7.11	—	—	Ion exchange	(235)
$Cd(C_2O_4)_2^{2-}$	5.77	25	→0	Solubility	(423)
	5.66	25	→0	Solubility	(81)
	5.64	—	—	Ion exchange	(235)
$Pb(C_2O_4)_2^{2-}$	6.54	26	→0	Solubility	(231, 287, 372)
$VO(C_2O_4)_2^{2-}$	9.76	—	0.05, pH 2.5	Spectrophotometric	(417)
$Al(C_2O_4)_3^{3-}$	16.3	—	→0	Potentiometric	(244, 245)
	9.68	32	0.01	Potentiometric	(126)
$Mn(C_2O_4)_3^{3-}$	19.42	25	2 M $HClO_4$	Kinetic	(407)
$Fe(C_2O_4)_3^{3-}$	21.6	—	—	Polarographic	(259)
	23.9	—	—	Polarographic	(416)
	20.2	—	—	Potentiometric	(247)
	17.96	25	0.5 M $NaClO_4$	Solubility	(366)
$Co(C_2O_4)_3^{3-}$	~20	—	—	—	(88)
$Y(C_2O_4)_3^{3-}$	11.47	25	→0	Solubility	(137)
$Ce(C_2O_4)_3^{3-}$	11.30	25	→0	Solubility	(94)
$Nd(C_2O_4)_3^{3-}$	>14	25	→0	Solubility	(94)
$Yb(C_2O_4)_3^{3-}$	>14	24	→0	Solubility	(93, 94)
$Co(C_2O_4)_3^{4-}$	9.7	~18	—	Polarographic	(363)
	8.13	—	—	Ion exchange	(142)
$Ni(C_2O_4)_3^{4-}$	~14	18	—	Polarographic	(363)
	8.51	25	1 M KNO_3	Potentiometric	(427)
$Zn(C_2O_3)_3^{4-}$	8.15	~18	—	Solubility	(243, 291, 363, 371, 394)
$Fe(C_2O_4)_3^{4-}$	5.22	25	0.5 M $NaClO_4$	Solubility	(360)
$Th(C_2O_4)_4^{4-}$	24.48	—	—	Potentiometric	(54)

TABLE 11 (*Continued*)

Oxalato Complex	Log K	Temperature	Conditions μ	Method	References
		°*C.*			
$UO_2H_2C_2O_4^{2+}$	2.57	25	—	Spectrophotometric, potentiometric	(192)
$UO_2(C_2O_4)_2^{2-}$	10.57	25	—	Spectrophotometric, potentiometric	(192)
$NpO_2(C_2O_4)^-$	3.30	—	—	Spectrophotometric	(175)
$NpO_2(C_2O_4)_2^{3-}$	3.78	—	—	Spectrophotometric	(175)
$Pu(C_2O_4)_2^-$	7.94	70	—	Solubility	(152)
	9.31	20	—	Solubility	(152)
	9.15	—	—	Ion exchange	(153)
$Pu(C_2O_4)_4^{3-}$	8.25	70	—	Solubility	(152)
	9.39	20	—	Solubility	(152)
	10.66	25	1 *M* $K_2C_2O_4$	Polarographic	(143)
$Pu(C_2O_4)_4^{5-}$	8.60	70	—	Solubility	(152)
	9.92	20	—	Solubility	(152)
	11.62	25	1 *M* $K_2C_2O_4$	Polarographic	(143)
$Pu(HC_2O_4)_4^-$	10.96	—	—	Ion exchange	(153)
$Pu(C_2O_4)^{2+}$	8.75	20	—	Solubility	(299)
$Pu(C_2O_4)_3^{2-}$	23.40	20	—	Solubility	(152)
$Pu(C_2O_4)_4^{4-}$	27.48	25	1 *M* $K_2C_2O_4$	Polarographic	(143)
	27.48	20	—	Solubility	(299)
$PuO_2(C_2O_4)_2^{2-}$	11.4	—	—	Solubility	(150)
$Am(C_2O_4)_2^-$	9.8	—	—	Ion exchange	(300)
$Am(HC_2O_4)_4^-$	11.0	—	—	Ion exchange	(300)

μ = ionic strength; →0 = approaching zero μ; K refers to cumulative or gross stability constants: $M + nL = ML_n$.

$$K = \frac{(ML_n)}{(M)(L)^n}$$

However, a hydrolytic reaction of the type

$$2H_2O + M(C_2O_4)_4^{4-} = M(C_2O_4)_3(H_2O)(OH)^{3-} + HC_2O_4^- + H^+$$

seems to be a general feature for the tetraoxalates of thorium(IV), uranium(IV), zirconium(IV), and hafnium(IV) (214). A low pH is therefore preferred when the tetraoxalates are being prepared. One of the insoluble products of the complete hydrolysis of $K_4Th(C_2O_4)_4$ has been identified as $K_2Th_2(C_2O_4)_5$, and it is very likely that the following equilibrium may be present along with complete or partial dissociation to free Th^{4+} ion (54):

$$2Th(C_2O_4)_4^{4-} = Th_2(C_2O_4)_5^{2-} + 3C_2O_4^{2-}$$

Similar potentiometric measurements made while adding oxalate ion to the zirconyl ion indicate the formation of di-, tetra-, hexa-, and octaoxalatozirconium(IV) complexes (52, 295).

(g) Polarographic method

Investigation of inorganic complex ions by the polarographic method has been reviewed earlier (149, 259). Titanium(III) and titanium(IV) yield (327) reversible polarographic waves in oxalic acid solutions at pH < 3. The $E_{1/2}$ in volts vs. the standard calomel electrode is expressed as:

$$E_{1/2} = -0.25 - 0.080\,\text{pH} + 0.020\log[H_2C_2O_4]$$

being independent of titanium concentration. The electrode reaction can be written as:

$$TiO(C_2O_4)_2^{2-} + 2H^+ + e^- = Ti(C_2O_4)_2^- + H_2O$$

and the $E_{1/2}$, extrapolated to 1 *M* oxalic acid and pH 0, is −0.25 v. vs. the standard calomel electrode or 0 v. vs. the standard hydrogen electrode (*cf.* E^0 for Ti^{3+}-TiO^{2+} ca. −0.04 v. vs. the standard hydrogen electrode). The slight shift of 0.04 v. shows that the stability constants of $TiO(C_2O_4)_2^{2-}$ and $Ti(C_2O_4)_2^-$ are not very different from each other, although no absolute values were obtained in this study. However, in the same paper, some spectrophotometric measurements on the yellow titanium(III) oxalato complex at 390 mμ are reported which indicate the formula $Ti(C_2O_4)_2^-$.

Some new spectrophotometric and conductometric studies (398) on the $TiOC_2O_4^-$ ion give a value of 2.161×10^{-8} for the stability constant at 23°C. The colorless titanium(IV) oxalato complexes have also been studied recently (25) by measurement of the optical density of the solutions in the ultraviolet region. At pH $\leqslant 1$ the main species is $TiOC_2O_4^0$ ($K_{\text{diss.}} = 2.5 \times 10^{-7}$), and as the pH increases $TiO(C_2O_4)_2^{2-}$ ($K_{\text{diss.}} = 5 \times 10^{-4}$) forms. Titanium is not precipitated as the hydroxide in oxalate media at pH's below 5.

Studies on the polarographic characteristics of vanadium(II), vanadium(III), vanadium(IV), and vanadium(V) in oxalate media enabled partial identification of the oxalato complexes. The variations of the observed $E_{1/2}$ with oxalate concentration in the vanadium(II),(III)-oxalate system indicate the couple:

$$V(C_2O_4)_p^{3-2p} + e^- = 2C_2O_4^{2-} + V(C_2O_4)_{p-2}^{6-2p}$$

with an E^0 value of −0.89 v. vs. the standard hydrogen electrode in solutions of pH ~4.5 (261). Vanadium(IV) has been reported to form a complex with the $HC_2O_4^-$ ion (456) (see Section III,C,1,(a)).

Extensive investigation of the iron(II),(III)-oxalate system (259, 260, 366, 394, 416) offers conclusive evidence for the ions $Fe(C_2O_4)_2^{2-}$, $Fe(C_2O_4)_3^{4-}$, and $Fe(C_2O_4)_3^{3-}$ (see table 11 for the stability constants).

Polarographic study of the copper(II)-oxalate system resulted in new thermodynamic data (286) for several polynuclear basic oxalato complexes of copper(II) such as $[Cu_4(OH)_6(C_2O_4)]^0$. The standard potential for the half-cell reaction,

$$Cu + 2C_2O_4^{2-} = Cu(C_2O_4)_2^{2-} + 2e^-$$

is −0.04 v. The stability constant for $Cu(C_2O_4)_2^{2-}$ is listed in table 11.

Polarographic and spectrophotometric data on the oxalato complexes of niobium and tantalum in aqueous solutions indicate the existence of +3 and +4 oxidation states of these elements, possibly as their oxalato complexes (130).

The ion $Pb(C_2O_4)_2^{2-}$ is reported to be stable in aqueous solution (288) at pH 7.4–10.7, and the $E_{1/2}$ value of −0.581 ± 0.002 v. agrees well with the value calculated from the dissociation constant determined earlier by the solubility method (231). At pH ~12, a basic oxalate of the formula $3Pb(OH)_2 \cdot PbC_2O_4$ precipitates from oxalate solutions (0.05 *M*). The reaction is:

$$4HPbO_2^- + 4H_2O + C_2O_4^{2-} = 3Pb(OH)_2 \cdot PbC_2O_4 + 6OH^-$$

The equilibrium constant for this reaction is given as 1.9×10^3 (288).

(h) Other methods

Abnormally low Λ_∞ values were observed in some early studies of solubility and *electrical conductance* of systems containing oxalate and magnesium(II), manganese(II), cobalt(II), nickel(II), zinc(II), and cadmium(II) (372) and were explained in terms of complex formation. The conductance method (189, 237, 274) has been applied to the detection of the complex ions $Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)(H_2O)_4^+$ (385). Conductance studies on mixtures of Na_2MoO_4 and $Na_2C_2O_4$ at pH 7.64–8.50 indicate the presence of $MoO_3(C_2O_4)_2^{2-}$ (339, 340), but this has been questioned recently because of observations on the same system which indicate only a 1:1 complex between molybdate(VI) and oxalate (382, 404) (see also Section III,C,1,-(a)).

Electrophoresis has been employed to demonstrate the presence of the oxalato complex of magnesium(II) (297), but no quantitative determination of the stability constant was made or claimed. However, the relative tendency of magnesium(II) to form complexes with carboxylate ions was determined as oxalate > citrate > tartrate.

By a *thermometric titration* procedure (55) using fairly concentrated solutions of thorium(IV) nitrate and potassium oxalate, which give an appreciable rise in temperature on mixing, observations were made which indicate complexes of the types $Th(C_2O_4)_3^{2-}$, $Th(C_2O_4)_4^{4-}$, and $Th_2(C_2O_4)_5^{2-}$. Data in the same paper on the depression of the freezing point of mixtures of thorium(IV) nitrate and potassium oxalate and on the results of a *cryoscopic titration* confirm the complex ions $Th(C_2O_4)_3^{2-}$ and $Th(C_2O_4)_4^{4-}$.

Several zirconium oxalato complexes have been reported in a systematic *study of the phases* which separate on mixing $ZrOC_2O_4$, $M_2C_2O_4$, and H_2O at various temperatures; these have been reviewed in a textbook (52).

Study of complex formation in solutions by the *proton magnetic resonance method* has been discussed recently (351). Data are given for $Fe(C_2O_4)_3^{3-}$, including a description of a method for determining the stability constant.

Using certain *displacement reactions* a method has been developed for obtaining the stability constants of $FeC_2O_4^+$, $Fe(C_2O_4)_2^-$, and $Fe(C_2O_4)_3^{3-}$ (20, 21). The decrease in intensity of the colored complexes $FeSCN^{2+}$ and Fe-salicylate^{2+} in the presence of the oxalate ion is stated to result from the reactions:

$$FeSCN^{2+} + HC_2O_4^- = FeC_2O_4^+ + HSCN$$

$$\text{Fe-sal}^{2+} + HC_2O_4^- = FeC_2O_4^+ + \text{H-sal}$$

These can be followed spectrophotometrically, and from a knowledge of the stability constants of the $FeSCN^{2+}$ and Fe-sal^{2+} complexes it has been possible to calculate the stability constant for $FeC_2O_4^+$. At pH $\leqslant 1$ $FeC_2O_4^+$ is the main species. At pH 2.5 $Fe(C_2O_4)_2^-$ predominates, and at a higher pH and in the presence of excess oxalate the main species is the $Fe(C_2O_4)_3^{3-}$ ion. The dissociation constant for the ion $FeC_2O_4^+$ determined by the study is 2.2×10^{-8}; this is in fair agreement with the independently obtained value of 0.7×10^{-8} from optical densities in the ultraviolet region of isomolar solutions containing iron(III) perchlorate and oxalic acid at different acidities. The stepwise dissociation constants for $Fe(C_2O_4)_2^-$ and $Fe(C_2O_4)_3^{3-}$ obtained in the equilibrium study above were 1.6×10^{-6} and 5×10^{-8}, respectively.

2. Stability-constant data

The stability-constant data are shown in table 11. No quantitative general conclusions can be drawn, although a marked decrease in the stability constant is noticeable for all the tripositive metal oxalato complexes: $M(C_2O_4)_3^{3-}$, $M(C_2O_4)_2^-$, and $MC_2O_4^+$. Qualitative predictions regarding the stability of the complex and the number of *d* electrons in the first transitional series apparently can be made for the oxalato complexes of manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II). Thus, in $M(C_2O_4)_2^{2-}$ the stability increases in the order iron(II), cobalt(II), and nickel(II) (see table 11), as predicted earlier (173).

The complexes of the alkaline earth metals show an increasing trend in stability with increasing charge²/radius ratio:

Complex	Log K_1 (18°C., μ = 0)	e^2/r
$Mg(C_2O_4)_2^{2-}$	↑ 3.43 (99a)	↑ 8.13
$Ca(C_2O_4)_2^{2-}$	~3 (245)	4.05
$Sr(C_2O_4)_2^{2-}$	2.54 (296, 371)	3.15
$Ba(C_2O_4)_2^{2-}$	~2.3 (296)	2.79

$$K_1 = \frac{[M(C_2O_4)_2^{2-}]}{(MC_2O_4^0)(C_2O_4^{2-})}$$

In the absence of more comprehensive and reliable data on the stability constants of the oxalato complexes, any other correlations would be only speculative and qualitative.

D. REACTIONS AND REACTION KINETICS

Since in oxalato complexes the linkage between the ligand and the metal is via oxygen atoms, studies of reaction kinetics yield substantial data on the general nature of this M—O coördinate bond. In this section are discussed the kinetics of the various types of reactions undergone by oxalato complexes which are pertinent to this purpose.

1. Isomerization processes

Two independent studies (98, 184) on the kinetics of the trans-cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ have been made, using a spectrophotometric method (176, 225). At 415 mμ the cis form absorbs considerably more (see table 2) than the trans form and the kinetics show that the rate of the trans-cis conversion is first order with respect to the concentration of the $Cr(C_2O_4)_2(H_2O)_2^-$ ion, independent of added hydrogen ion (pH 1.85–4.28), and slightly dependent on the ionic strength. The free energy, enthalpy, and entropy of activation are 22.1 kcal. mole^{-1}, 17.5 kcal. mole^{-1}, and -15.3 e.u., respectively. The proposed mechanism involves an intermediate with three molecules of water present in the chromium octahedron:

$$\text{trans} + H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} [\text{intermediate}] \underset{k_4}{\overset{k_3}{\rightleftarrows}} \text{cis} + H_2O$$

This mechanism explains not only the trans-cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ but also the exchange of H_2O for Cl in the $CrCl_2(H_2O)_4^-$ ion, as evidenced by the almost identical $\Delta S^\ddagger$ value of -16.3 e.u. for the latter reaction (188). A reasonable assumption is that k_2 and $k_3 \gg k_1 \gg k_4$, which is consistent with the high negative entropy of activation (184).

Recently it has been shown (369) that below pH 2 an acid-catalyzed reaction contributes to the rate according to the law

$$\text{Rate} = (k_1 + k_2(H^+)^{1.5})(\text{complex})$$

No explanation of the apparent 1.5 power for the dependence on hydrogen-ion concentration has been proposed as yet, but over a limited range this may simply be a combination of first- and second-order effects, as found for the aquation of $Cr(C_2O_4)_3^{2-}$ in acid solution (238).

Similar studies on the kinetics of trans-cis isomerization in other systems would be interesting in understanding the role of solvent water and of (H^+) in the mechanism. Although no kinetic study has been made on the $Mn(C_2O_4)_2(H_2O)_2^-$ ion, two crystalline solids of the same composition, $KMn(C_2O_4)_2(H_2O)_2{\cdot}3H_2O$, a golden yellow and a green form, have been isolated (74). Spectral evidence makes it likely that the yellow form is the cis isomer and the green form the trans isomer, and it is assumed that in solution, a rapid equilibrium between the cis and trans isomers is established. The $Mn(C_2O_4)_2(H_2O)_2^-$ ion is, however, less stable than $Cr(C_2O_4)_2(H_2O)_2^-$. While the corresponding bisoxalatodiaquo compounds of iron(III) (429), indium(III) (292), and iridium(III) (118) have been reported, no attempt has been made to separate the cis and trans isomers.

2. Optical activity and kinetics of racemization

Werner was the first to demonstrate the feasibility of resolving an oxalato complex when he succeeded in preparing the optical antipodes of $K_3Cr(C_2O_4)_3$ by fractional crystallization of the active strychnine derivatives (436). Since that time, more studies have been made of methods of resolution and kinetics of racemization of oxalato complexes than of any other specific class of coördination compounds. Much of this work has been recently reviewed in detail in two textbooks (27, 39). Several methods of resolution have been successful with the oxalato complexes other than the diastereoisomer technique already mentioned, and include spontaneous crystallization of antipodes (204), preferential crystallization (440), and the "method of active racemates" (106). A further interesting possibility is the hitherto unconfirmed use of the selective decomposition of a photosensitive complex by means of circularly polarized light, which has been reported to result in the partial resolution of $K_3Co(C_2O_4)_3$ (419). It now appears certain that for complexes of the type $M(C_2O_4)_3^{x-}$ only the nonlabile species with M = chromium(III), cobalt(III), germanium(IV), iridium(III), or rhodium(III) are resolvable, while the labile complexes with M = aluminum(III), manganese(III), iron(III), or gallium(III) are not, despite some unconfirmed contrary claims (39). Other resolvable species include $K[Cr(en)(C_2O_4)_2]$, $[Cr(en)_2C_2O_4]Cl$, $[Co(en)_2C_2O_4]Cl$, and $K_3[Ir(C_2O_4)_2Cl_2]$.

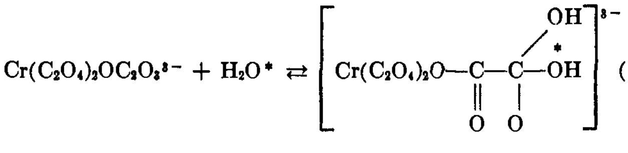
The most widely studied oxalato complex ion is $Cr(C_2O_4)_3^{3-}$. Its racemization rate is first order in complex concentration and is markedly accelerated by acid, alkali, or inert salts (43). Anions other than OH^-

have little effect on the rate, as expected for an anionic complex. Cations, however, show marked specific accelerating effects, the effect increasing with concentration of a given ion and being greatest for multicharged ions. Similar cationic acceleration has been observed for $Co(C_2O_4)_3^{3-}$ and $[Cr(en)(C_2O_4)_2]^-$ but is of much smaller magnitude (66). The activation energy for the racemization of $Cr(C_2O_4)_3^{3-}$ in water has been given widely divergent values, but the recently reported figure of 13.3 kcal. mole^{-1} appears to be the most reliable (379). These latter workers also investigated the effect of solvent composition on the rate of racemization. They confirmed earlier reports (66, 436) of decrease in rate with increasing proportion of acetone in acetone-water mixtures, and extended the study to include methanol, ethanol, 1-propanol, 2-propanol, and dioxane, with similar results. No definite correlations were established.

There has been much speculation concerning the mechanism of racemization of the resolvable trisoxalato complexes. Early isotopic tracer studies (265, 266) established that oxalate exchange with the chromium(III) and cobalt(III) analogs is much slower than racemization, ruling out any complete parallelism between the mechanisms of the two processes.

A recent detailed study of the $Cr(C_2O_4)_3^{3-}$–$\overset{*}{C}_2O_4^{2-}$ exchange reaction in aqueous solution (166) showed that the racemization is about 2000 times as fast as the exchange under similar conditions. Further insight into the mechanism of the racemization is offered by the work of Carter and Llewellyn (71), who studied O^{18} exchange between $Cr(C_2O_4)_3^{3-}$ and labeled solvent water. This process is acid-catalyzed and occurs at a rate slower than but within an order of magnitude of the racemization rate under comparable conditions. The mechanism suggested for oxygen exchange is a rapid one-ended dissociative equilibration of coördinated oxalate, accompanied by a slower exchange of oxygen atoms with the solvent through a hydrated ortho-oxalate intermediate, viz.

$$Cr(C_2O_4)_3^{3-} \rightleftharpoons Cr(C_2O_4)_2OC_2O_3^{3-} \qquad (i)$$



$$Cr(C_2O_4)_2OC_2O_3^{3-} + H_2O^* \rightleftharpoons \left[Cr(C_2O_4)_2O{-}\underset{\overset{\|}{O}}{C}{-}\underset{\overset{|}{O}}{\overset{OH}{C}}{-}\overset{*}{O}H \right]^{3-} \qquad (ii)$$

Step (i) can account for the very rapid rate of racemization if it is assumed that intramolecular inversion of configuration occurs easily for the monodentate intermediate. Further support of this type of interpretation is offered by recent work (238) on the acid-catalyzed aquation of $Cr(C_2O_4)_3^{3-}$, in which studies of the solvent deuterium isotope effect provided strong support for a rapid preëquilibration step of the form:

$$Cr(C_2O_4)_3^{3-} + H_3O^+ \rightleftharpoons Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-} \qquad (iii)$$

This reaction can accommodate both racemization and oxygen exchange in a manner similar to that outlined above and has the advantage of explaining the observed acid catalysis of both these processes. The cationic catalysis and organic solvent effect mentioned earlier also can be fitted reasonably, if qualitatively, into this picture, since reaction (iii) would be expected to be accelerated by high ionic strength and decelerated by reduction of water concentration. The recently observed photoracemization of $Cr(C_2O_4)_3^{3-}$ (8) also conforms to these general views if it is assumed that the main chemical result of the photoactivation is breakage of one Cr—O bond, as in reaction (i).

It is of interest that the mechanism of loss of optical activity of the ion $Co(en)_2C_2O_4^+$ bears little or no resemblance to that of the trisoxalato species. A recent study (289) shows that the reaction becomes measurable in the presence of alkali at elevated temperatures, that it is in fact, a decomposition, as suggested by earlier work (66), and that it proceeds according to the mechanism:

$$Co(en)_2C_2O_4^+ + OH^- \rightleftharpoons Co(en)_2OC_2O_3 \cdot OH \quad \text{(rate determining)} \qquad (iv)$$

$$Co(en)_2OC_2O_3 \cdot OH + OH^- \rightleftharpoons \textit{cis-}Co(en)_2(OH)_2^+ + C_2O_4^{2-} \quad \text{(fast)} \qquad (v)$$

$$\textit{cis-}Co(en)_2(OH)_2^+ \rightleftharpoons \textit{trans-}Co(en)_2(OH)_2^+ \quad \text{(fast)} \qquad (vi)$$

It may be that reactions (iv) and (v) amount only to a mutarotation, but complete loss of activity results from reaction (vi) in any case. Confirmation of this mechanism is afforded by the fact that the kinetic characteristics of the base-catalyzed oxalate exchange (studied by means of $C_2^{14}O_4^{2-}$) and of the spectrophotometrically observed decomposition reaction are identical with those of the "racemization." The contrast between the behavior of $Coen_2C_2O_4^+$ and that of the trisoxalato complex may possibly be ascribed to the existence of strong N—H—O hydrogen bonding in the former, as suggested in recent deuterium-exchange studies (38, 51, 250).

Finally, it should be noted that a few measurements of optical rotatory dispersion have been made on the trisoxalato complexes. Jaeger (204) obtained the curves for the chromium(III), cobalt(III), rhodium(III), and iridium(III) analogs and noted their similarities. Later workers (213) reinvestigated the cobaltiate and interpreted their data in terms of Kuhn's theory of optical rotatory dispersion (241), which has been recently reviewed (239).

A discussion has also appeared concerning the use of data on optical rotatory dispersion in the determination of the absolute configuration of the $Co(C_2O_4)_3^{3-}$ ion (240, 242). Further work in this field should prove quite fruitful.

3. *Ligand substitution and exchange reactions*

Ligand substitution and exchange reactions have been recently reviewed in two textbooks both as regards general properties of octahedral and square planar complexes (39) and more specifically as regards the complexes of the transition metals (396). The two important types of substitution reactions with reference to the oxalato complexes are (*a*) reactions in which *oxalate* is the leaving group and (*b*) reactions in which *oxalate* is the entering group. Isotopic exchange reactions using *labeled oxalate* are treated separately as subsection (*c*), since the oxalate can be visualized as both entering and leaving the complex with one or more steps involved.

(a) Reactions in which oxalate is the leaving group

The most common in this type are those involving replacement of oxalate by the solvent itself, usually water molecules. For example, the kinetics of aquation of the $Cr(C_2O_4)_3{}^{3-}$ ion have been studied as a function of complex-ion concentration, acidity, added oxalic acid, temperature, and D_2O solvent composition using a spectrophotometric method (238). The mechanism proposed was:

$$Cr(C_2O_4)_3{}^{3-} + H_3O^+ \rightleftarrows Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-}$$

$$Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-} + H_2O \rightleftarrows Cr(C_2O_4)_2(H_2O)_2{}^- + HC_2O_4{}^-$$

$$Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-} + H_3O^+ \rightleftarrows Cr(C_2O_4)_2(H_2O)_2{}^- + H_2C_2O_4$$

The above mechanism is consistent with the observed rate law:

$$-d[Cr(C_2O_4)_3{}^{3-}]/dt = k'(H_3O^+)[Cr(C_2O_4)_3{}^{3-}] + k''(H_3O^+)^2[Cr(C_2O_4)_3{}^{3-}]$$

The mixed order with respect to the H_3O^+ ion is interpreted in terms of a rapid preëquilibration of complex with one proton, followed by parallel rate-determining reaction paths involving either noncatalyzed or acid-catalyzed displacement of oxalate. Experiments in H_2O/D_2O solvent mixtures showed that the rate of aquation increased as a function of the deuterium-atom fraction, in agreement with the Gross–Butler equation (157, 337) (see table 12). The calculated k_n/k_H ratio was obtained from Purlee's modified Gross–Butler equation, using his tabulation of values for the $Q'(n)$ function and the equilibrium constant L at 50°C. The good agreement between the observed and calculated values for k_n/k_H can be taken as strong support for the mechanism of general acid catalysis:

$$S + H^+ \rightleftarrows SH^+;\ SH^+ \rightarrow \text{products}$$

with the second step rate-determining but not subject to isotope effect (444). This is exactly the type of mechanism proposed for the acid-catalyzed aquation of $Cr(C_2O_4)_3{}^{3-}$.

TABLE 12

Solvent deuterium isotope effect on the aquation of $Cr(C_2O_4)_3{}^{3-}$
Data from Krishnamurty and Harris (238)

$n =$ (D)/(H + D)	$k_{exp.}$	k_n/k_H (Observed)	k_n/k_H (Calculated)
	sec.$^{-1}$ × 10^4		
0.00	6.8	1.00	1.00
0.26	7.7	1.13	1.24
0.49	10.1	1.49	1.52
0.91	16.0	2.35	2.38
1.00	17.8*	2.62	(2.62)

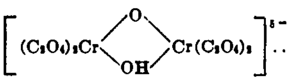
* Graphically extrapolated value.

The analogous acid-catalyzed aquation of $Rh(C_2O_4)_3{}^{3-}$ is markedly different, however. Aquation is very slow at room temperature. The half-time is of the order of 1 hr. at 80°C. in 1 *M* perchloric acid (36). (Under these conditions aquation of $Cr(C_2O_4)_3{}^{3-}$ is complete in a few seconds.) The rate is found to be first order in concentration of $Rh(C_2O_4)_3{}^{3-}$ ion. It is near first order in (H^+) ion at low acidities but at higher $(HClO_4)$ the order increases with increasing concentration of perchloric acid, somewhat after the fashion of cases where Hammett's *H* function applies. Complete interpretation of this work has not yet been made.

A summary of the data on several aquation reactions is presented in table 13. It can be pointed out in the case of manganese(III) oxalato complexes that the tendency to undergo aquation decreases with increasing number of ligands attached to the central metal ion. This is in direct contrast to the chromium(III) and rhodium(III) complexes, where only the trisoxalato

TABLE 13

Rates of aquation of oxalato complexes

Oxalato Complex	k	Temperature	$E_{act.}$	$\Delta S^\ddagger$	Reference
	min.$^{-1}$	*°C.*	*kcal. mole*$^{-1}$	*e.u.*	
$Cr(C_2O_4)_3{}^{3-}$	3.9×10^{-3}	50	22.1	−15	(238)
	1.0×10^{-5}	25	12	−37	(165)
$MnC_2O_4{}^+$	11.8	25	18.3	−2	(408)
$Mn(C_2O_4)_2{}^-$	4.6×10^{-3}	25	—	—	(408)
$Mn(C_2O_4)_3{}^{3-}$	2.1×10^{-3}	25	22.4	−1	(408)
$Co(C_2O_4)_3{}^{3-}$	4.3×10^{-4}	25	34	30	(88)
$Rh(C_2O_4)_3{}^{3-}$	41.6	80	—	—	(36)

form aquates at the measurable rate under moderate conditions (36, 238).

Equilibrium studies by the spectrophotometric method confirm the existence of mixed complexes of the type: $[Cu(C_2O_4)en]^0$ (107), $[Ni(C_2O_4)en]^0$, $[Ni(C_2O_4)en_2]^0$, and $[Ni(C_2O_4)_2en]^{2-}$ (427). These are formed as a result of the substitutions:

$$Cu(C_2O_4)_2^{2-} + en \rightleftarrows [Cu(C_2O_4)en]^0 + C_2O_4^{2-}$$

$$Ni(C_2O_4)_2^{2-} + en \rightleftarrows [Ni(C_2O_4)en]^0 + C_2O_4^{2-}$$

$$Ni(C_2O_4)_3^{4-} + en \rightleftarrows [Ni(C_2O_4)_2en]^{2-} + C_2O_4^{2-}$$

Neither the rate of oxalate elimination or a plausible mechanism for the formation of the mixed complexes cited above is presently known. However, in the same studies, the overall stability constants of the mixed complexes in terms of equilibria with the aquo metal ion, the oxalate ion, and ethylenediamine are given precisely and are listed in table 14.

TABLE 14

Stability constants of mixed oxalato complexes

Mixed Complex	Log *K*	Conditions
$[Cu(C_2O_4)en]^0$	15.44 ± 0.14	1 *M* $NaNO_3$, 25°C.
$[Ni(C_2O_4)en]^0$	11.29 ± 0.10	1 *M* KNO_3, 25°C.
$[Ni(C_2O_4)en_2]^0$	16.15 ± 0.06	1 *M* KNO_3, 25°C.
$[Ni(C_2O_4)_2en]^{2-}$	13.02 ± 0.08	1 *M* KNO_3, 25°C.

(b) Reactions in which oxalate is the entering group

Several reactions which form oxalato complexes may be treated as substitution reactions in which the oxalate group enters the coördination sphere of an aquo metal ion or replaces another ligand:

$$M(H_2O)_x^{+n} \rightarrow M(H_2O)_{x-2}(C_2O_4)^{+n-2} \rightarrow M(H_2O)_{x-4}(C_2O_4)^{+n-4} \rightarrow$$

or

$$M(H_2O)_xL_y^{+n} \rightarrow M(H_2O)_xL_{y-2}(C_2O_4)^{+n-2} \rightarrow \ldots$$

The successive substitutions generally take place in steps that are identifiable, as in the case of Mn_{aq}^{III}-oxalate and $Cr(H_2O)_6^{3+}$-oxalate systems, which have been extensively investigated. Whereas equilibrium studies indicate the stability of the species, rate data enable postulation of a reasonable mechanism for the substitution process, as illustrated below.

The manganese(III) oxalato complexes have been the subject of several types of investigations: preparative studies (73), equilibrium studies (74), rate studies (120, 121), oxidation-reduction studies (405, 406, 408), as intermediates in the permanganate-oxalic acid reactions (252-254, 258), and isotopic exchange studies (6, 336). Various features of these studies have recently been thoroughly reviewed (246).

The kinetics of the reaction between $Cr(H_2O)_6^{3+}$ and $C_2O_4^{2-}$ have been followed by polarographic, conductometric (185), and spectrophotometric (187) methods. The following tentative mechanism consistent with rate data has been suggested for the oxalate chelation reactions. The additional observation that the rate of addition of acetate ion to chromium(III) is nearly the same as the rate of addition of oxalate ion shows that the slow step must be breakage of a Cr—OH_2 or formation of a Cr—O bond rather than completion of the chelate ring (186).

$$Cr(H_2O)_6^{3+} + C_2O_4^{2-} \rightarrow Cr(C_2O_4)(H_2O)_5^{+} \qquad \text{(rapid?)}$$

$$Cr(C_2O_4)(H_2O)_5^{+} \rightleftarrows Cr(C_2O_4)(H_2O)_4(OH)^0 + H^+ \qquad (K = 1.0 \times 10^{-6})$$

$$Cr(C_2O_4)(H_2O)_4(OH)^0 \xrightarrow[-H_2O]{k_1} Cr(C_2O_4)(H_2O)_3(OH)^0 \qquad \text{(slow)}$$

$$Cr(C_2O_4)(H_2O)_3(OH)^0 + H^+ \rightleftarrows Cr(C_2O_4)(H_2O)_4^{+}$$

$$Cr(C_2O_4)(H_2O)_4^{+} \xrightarrow{C_2O_4^{2-}} Cr(C_2O_4)_2(H_2O)_3^{-} \qquad \text{(rapid)}$$

$$Cr(C_2O_4)_2(H_2O)_3^{-} \xrightarrow[-H_2O]{k_2} Cr(C_2O_4)_2(H_2O)_2^{-} \qquad \text{(slow)}$$

The third chelation step to form $Cr(C_2O_4)_3^{3-}$ appears to proceed in the same way, and the rate is found to be independent of pH over the range 4.0-9.3 (187). A summary of rate data is presented in table 15.

Substitution of oxalate in *trans*-$Pt(NH_3)_2Cl_2$ has been studied recently. At 25°C., 5×10^{-4} *M* in complex ion, and 0.01 *M* in oxalate ion, the rate constant is 4.8×10^{-3} min.$^{-1}$ All other conditions being the same, the rate constant is found to nearly double if the oxalate-ion concentration is doubled (30).

(c) Isotopic exchange studies

The application of the isotopic exchange technique in understanding the nature of inorganic complexes in solution is discussed at length in a recent review (397). The available data on oxalate complexes are summarized in table 16. Thorough kinetic investigations

TABLE 15

Rates of oxalate substitution

Reaction	*k*	Temperature	ΔH^{+}	$\Delta S^{\ddagger}$	Reference
	sec.$^{-1}$	°*C.*	*kcal. mole*$^{-1}$	*e.u.*	
$Cr(H_2O)_4^{3+} + C_2O_4^{2-}$	2.82×10^{-3}	25	23.2	7.5	(185)
$Cr(C_2O_4)(H_2O)_4^{+} + C_2O_4^{2-}$	3.10×10^{-4}	25	23.7	4.4	(185)
$Cr(C_2O_4)_2(H_2O)_2^{-} + C_2O_4^{2-}$	1.05×10^{-4}	40	22.6	−4.2*	(187)

* $\Delta S^{\ddagger}$ value in reference 187 reads as 4.2, owing to a typographical error since checked with the authors.

TABLE 16

Isotopic exchange studies

Reaction	Conditions			Observed Exchange	References
	Reactant Concentration	pH	Temperature		
	M		°*C.*		
$Al(C_2O_4)_3^{3-} + C_2^*O_4^{2-}$	0.03, 0.015		25	~90% in 20 sec.	(266)
$Cr(C_2O_4)_3^{3-} + C_2^*O_4^{2-}$	0.06, 0.012		50	<5% in 25 min.	(265)
				Detailed kinetics	(166, 263)
$Cr(C_2O_4)_2(H_2O)_2^{-} + C_2^*O_4^{2-}$	0.05, 0.05	1	50	<5% in 6 hr.	(238)
$Cr(C_2O_4)_3^{3-} + Cr^*(H_2O)_6^{3+}$	0.010, 0.010, 0.025 $HClO_4$		Room temperature	1% in 72 hr.	(290)
$Cr(C_2O_4)_3^{3-} + Cr^*(H_2O)_4Cl_2^{+}$	0.005, 0.005, 0.05 $HClO_4$			⩽5% in 1 hr.	(290)
$Mn(C_2O_4)^{2-} + C_2^*O_4^{2-}$	—		—	—	
$Mn(C_2O_4)_3^{3-} + Mn^*(H_2O)_6^{2+}$	0.01, 0.005, 0.1 $H_2C_2O_4$			⩾95% in <5 sec.	(336)
$Fe(C_2O_4)_3^{3-} + C_2^*O_4^{2-}$	0.06, 0.012	4.5–6.0	35	⩾95% in <20 sec.	(80, 179, 266)
$Fe(C_2O_4)_3^{3-} + Fe^*(H_2O)_6^{3+}$	0.01, 0.01	2.5	17-20	⩾95% in 10 min.	(44, 178)
$Fe^*(C_2O_4)_3^{3-} + Fe(CN)_6^{4-}$		1.2		⩽5% in 10 min.	(179)
$Co(C_2O_4)_3^{3-} + C_2^*O_4^{2-}$	0.06, 0.012		35, 50	⩽5% in 25 min.	(266)
	0.035, 0.015	8	50	50% in 130 hr.	(166)
$Co(C_2O_4)_3^{3-} + Co^*(H_2O)_6^{2+}$	—		—	No exchange	(33)
$Ni^*(C_2O_4)_2^{2-} + Ni(CN)_4^{2-}$	0.007, 0.007	6–8		⩽5% in 9 min.	(267)
	0.007 in $K_2C_2O_4$				
$Ga(C_2O_4)_3^{3-} + C_2^*O_4^{2-}$	0.028, 0.028		Room temperature	⩾95% in 1 min.	(293)
$Ge(C_2O_4)_3^{2-} + C_2^*O_4^{2-}$	Predicted slow				(294)
$Rh(C_2O_4)_3^{3-} + C_2^*O_4^{2-}$	0.005, 0.007, 0.07 $NaClO_4$	7.3	133	50% in 5.8 hr.	(36)
				Detailed kinetics	
$Zr(C_2O_4)_4^{4-} + C_2^*O_4^{2-}$	0.01–0.11 each		23–25	⩾95% in <2 min.	(214)
$Hf(C_2O_4)_4^{4-} + C_2^*O_4^{2}$	0.02–0.15 each		25	⩾95% in <3 min.	(214)
$Th(C_2O_4)_4^{4-} + C_2^*O_4^{2-}$	0.1 each		25	⩾95% in <2 min.	(214)
$U(C_2O_4)_4^{4-} + C_2^*O_4^{2-}$	0.05–0.28 each		23	⩾95% in <2 min.	(214)

have been made only in a few cases, e.g., $Cr(C_2O_4)_3^{3-}$, $Co(C_2O_4)_3^{3-}$, and $Rh(C_2O_4)_3^{3-}$.

The kinetic characteristics of ligand exchange in $Cr(C_2O_4)_3^{3-}$ (166, 238) have recently been described in detail. Earlier qualitative experiments (265, 266) had shown that this ion as well as $Co(C_2O_4)_3^{3-}$ exchanges negligibly slowly at room temperature, in contrast to the rapidly exchanging aluminum(III) and iron(III) analogs. The rate law for the $Cr(C_2O_4)_3^{3-}/C_2^*O_4^{2-}$ exchange can be expressed as (166):

$$\text{Rate} = [Cr(C_2O_4)_3^{3-}] \times \{k_a + k_b(C_2O_4^{2-}) + k_c(H_3O^+) + k_d(H_3O^+)(C_2O_4^{2-})\}$$

$$\begin{aligned} \text{where}\quad k_a &= 1.1 \times 10^{-6}\ \text{sec.}^{-1} \\ k_b &= 1.1 \times 10^{-4}\ M^{-1}\ \text{sec.}^{-1} \\ k_c &= 1.8 \times 10^{-3}\ M^{-1}\ \text{sec.}^{-1} \\ k_d &= 2.6 \times 10^{-1}\ M^{-2}\ \text{sec.}^{-1}\ \text{(all at 75°C.)} \end{aligned}$$

A mechanism of exchange which is consistent (in the range pH 2–4) with this rate law is:

$$\left.\begin{array}{l} Cr(C_2O_4)_3^{3-} + H_2O \leftrightarrows \\ \qquad Cr(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^{3-} \\ Cr(C_2O_4)_3^{3-} + H_3O^+ \leftrightarrows \\ \qquad Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-} \end{array}\right\} \text{Preëquilibration steps}$$

$$\left.\begin{array}{l} Cr(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^{3-} + H_2O \leftrightarrows \\ \qquad Cr(C_2O_4)_2(H_2O)_2^{-} + C_2O_4^{2-} \\ Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-} + H_2O \leftrightarrows \\ \qquad Cr(C_2O_4)_2(H_2O)_2^{-} + HC_2O_4^{-} \end{array}\right\} \text{Aquation steps}$$

$$\left.\begin{array}{l} Cr(C_2O_4)_2 \cdot OC_2O_3 \cdot H_2O^{3-} + HC_2^*O_4^{-} \leftrightarrows \\ \qquad Cr(C_2O_4)_2 \cdot OC_2^*O_3 \cdot H_2O^{3-} + HC_2O_4^{-} \\ Cr(C_2O_4)_2 \cdot OC_2O_3H \cdot H_2O^{2-} + HC_2^*O_4^{-} \leftrightarrows \\ \qquad Cr(C_2O_4)_2 \cdot OC_2^*O_3H \cdot H_2O^{2-} + HC_2O_4^{-} \end{array}\right\} \text{Bimolecular exchange steps}$$

The initial protonation in the preëquilibration step, as well as the nonexchangeability of $C_2O_4^{2-}$ with $Cr(C_2O_4)_2(H_2O)_2^{-}$, has been confirmed in a subsequent study (238) by (*1*) experiments in solvent mixtures of D_2O and application of the Gross–Butler equation (see Section III,D,3,(a)) and (*2*) exchange experiments using labeled oxalate in the $Cr(C_2O_4)_2(H_2O)_2^{-}$–$C_2^*O_4^{2-}$ system. The kinetic picture convincingly confirms the earlier postulation (263) that one-ended dissociation of the chelated oxalate must be an important step in the several types of reactions undergone by the $Cr(C_2O_4)_3^{3-}$ ion.

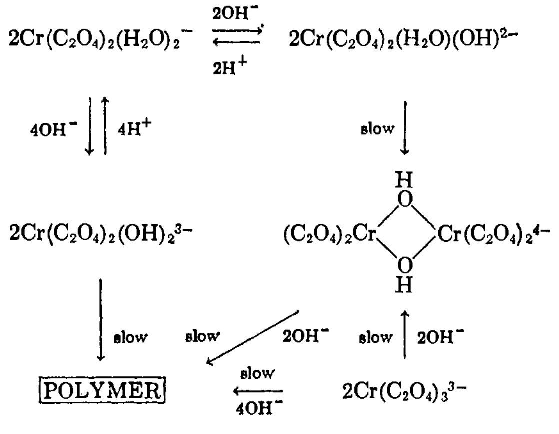
The thermal instability of $Co(C_2O_4)_3^{3-}$ is a deterrent factor which prevents conventional isotope-exchange studies. However, the exchange of $C_2O_4^{2-}$ with $Co(C_2O_4)_3^{3-}$ was followed semiquantitatively by precipitation and radioassay of the free oxalate as $CaC_2O_4 \cdot H_2O$ (166). Oxalate exchange proceeds at a rate negligible compared to that of thermal decomposition (the estimated half-time is ⩾ 130 hr. at 50°C. and pH 8, compared to 6.5 hr. for the thermal decomposition under these conditions). It is therefore confirmed that the decomposition proceeds by a mechanism not involving appreciable reversible equilibration of C_2O_4 radicals or ions. Other related studies on the electron-transfer exchange between $Co(C_2O_4)_3^{3-}$ and $Co(C_2O_4)_3^{4-}$ (7) and the photochemical and thermal decomposition studies (88, 99) are discussed in the appropriate sections.

The $C_2^*O_4^{2-}$ exchange with $Rh(C_2O_4)_3^{3-}$ is also of interest in that the latter does not undergo internal oxidation–reduction as does the corresponding $Co(C_2O_4)_3^{3-}$ ion. In its great resistance to water substitution it is significantly different from $Cr(C_2O_4)_3^{3-}$, as discussed in Section III,D,3,(a). The $Rh(C_2O_4)_3^{3-}$–

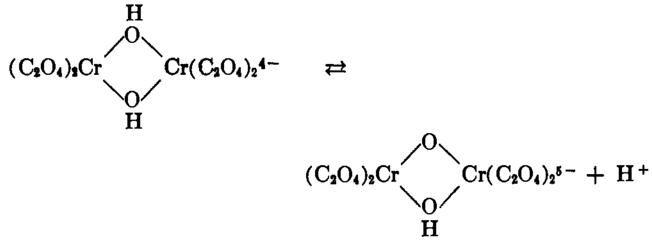
$\overset{*}{C}_2O_4^{2-}$ exchange has been studied (36) at 133°C. and pH 2.1-7.3 (room temperature acidities) in solutions buffered with $H_2C_2O_4$-$HC_2O_4^-$ and $HC_2O_4^-$-$C_2O_4^-$ and in unbuffered potassium oxalate. Both the total free oxalate and $Rh(C_2O_4)_3^{3-}$ were varied from 5.3×10^{-3} to 1.62×10^{-2} M at a constant ionic strength, 0.12. At pH 3.6, where the exchange rate is independent of acidity, the reaction was found to be first order in $Rh(C_2O_4)_3^{3-}$ and almost zero order in total oxalate. The first-order rate constant is 0.18 $hr.^{-1}$ Some preliminary experiments indicated an activation energy of ~24 kcal. $mole^{-1}$ for this constant. A mechanism analogous to the $Cr(C_2O_4)_3^{3-}$-$\overset{*}{C}_2O_4^{2-}$ exchange has been found to explain satisfactorily the rate data for the acid-catalyzed part of the exchange process. The acid-independent and the base-catalyzed parts require further investigation before the data on these processes can be completely interpreted.

4. Dimerization, addition, and polymerization

Recent kinetic studies by a spectrophotometric method (164) confirm earlier observations (438) concerning the formation of olated species from *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$ (see table 2 for pK values). On standing the hydroxy compounds, *cis*-$Cr(C_2O_4)_2(H_2O)(OH)^{2-}$ and *cis*-$Cr(C_2O_4)_2(OH)_2^{3-}$, partly dimerize irreversibly through the formation of "ol" or "diol" linkages and the following interrelations are observed (164):

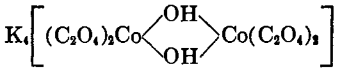


The rates of dimerization were obtained from the optical density data at 480 mμ, and the first-order rate constant for the slow step is 2.77×10^{-6} $sec.^{-1}$ at 25°C. and 0.10 ionic strength. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values corresponding to this constant and extrapolated to zero ionic strength are 22.5 kcal. $mole^{-1}$ and −8 e.u., respectively. The observed lower values for $\Delta H^{\ddagger}$ at higher ionic strengths are explained in terms of the ease with which a polar water molecule is lost in the initial dissociation process prior to dimerization (164). In an allied study (165) the same authors observed that the decomposition of the dimer by acid proceeds in two slow steps to form the $Cr(C_2O_4)_2(H_2O)_2^-$ ion. The residual basicity observed in the case of the dimer has been explained in terms of "oxolation":



The nature of the polymer that is formed in aged solutions of chromium(III) in oxalate solutions is not well understood, except that the analytical data indicate there to be three or four chromium atoms per molecule of the polymer.

An analogous study (7) on Durrant's salt (125) indicates that the compound has the binuclear structure,

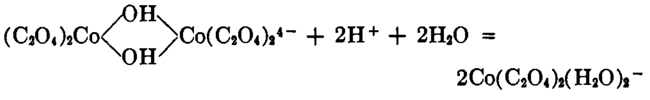


(328)

rather than

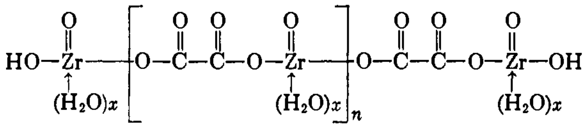
$K_2[Co(C_2O_4)_2(OH)(H_2O)]$

suggested first by Werner (439) and others (389). Solutions of the salt are neutral and the pH-titration behavior is best explained in terms of the reaction:



The pK of the dimer is reported as ~9 and that of the monomer as ~7.

The solubility of the white gelatinous zirconium(IV) oxalate in excess oxalate or ZrO^{2+} clearly indicates complex formation, and at least one polyoxalatopolyzirconic acid is reported (268):



An interesting discussion on these little-understood polymers is given in a recent textbook on zirconium (52). No kinetic studies apparently have been made of these systems as yet.

The behavior of many oxalato complexes in alkaline media has not been investigated and much work needs to be done on the nature of the products, their structure, and their reaction kinetics.

5. Oxidation-reduction processes, electrode-potential studies, and electron-exchange reactions

(a) Oxidation-reduction processes

Numerous investigations on the oxidation of oxalate ion by permanganate and associated studies dealing with the interaction of oxalate ion with manganese(III) have been recently summarized in a comprehensive review (246) and earlier in some critical surveys (3, 317). The overall disappearance of manganese(III) is given by the rate equation:

$$\begin{aligned} -\mathrm{d}(\mathrm{Mn(III)})/\mathrm{d}t &= k(\mathrm{Mn(III)}) \\ &= 2k_1(\mathrm{MnC_2O_4^+}) + 2k_2[\mathrm{Mn(C_2O_4)_2^-}] + 2k_3[\mathrm{Mn(C_2O_4)_3^{3-}}] \end{aligned}$$

The factor 2 in the rate expression is introduced to account for the rapid reaction observed between a reducing intermediate (CO_2^-, $C_2O_4^-$, or Mn^+) that is formed in the rate-determining step and a second manganese(III) ion, for example,

$$\mathrm{Mn(III)} + \mathrm{C_2O_4^-} \rightarrow \mathrm{Mn(II)} + 2\mathrm{CO_2} \quad (408)$$

That the various manganese(III) oxalato complexes participate in the reaction was shown by carrying out the study under varying acid and oxalate concentrations. In fact, this is the basis for a kinetic method of determining the stability constants of these complexes (see Section III,C,2). In an independent study (120) the kinetics of oxalate decomposition by manganese(III) have been explained in terms of an activated complex containing a disrupted C—C bond, the resonance form of which decomposes via internal electron transfer to manganese(II), carbon dioxide, and a radical-ion. The radical-ion that keeps the chain operating in the reaction is said to be $C_2O_4^-$. Earlier postulations of "active oxalic acid" (2, 3, 4, 269, 431) are better explained in terms of this radical-ion and are well discussed in the review cited (246).

The catalysis by several metal ions of oxalate oxidation reactions is likewise explained in terms of plausible participation of the metal oxalato complex. For example, the rate of oxidation of oxalic acid by chlorine is affected by cations such as VO^{2+}, Ce^{3+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ni^{2+}, and Pr^{3+} (405). In the reduction of chromium(VI) to chromium(III) by oxalate, the monoöxalato ion, $Cr(C_2O_4)(H_2O)_4^+$, has been postulated as an intermediate heat-stable complex which is converted to the bisoxalato ion, $Cr(C_2O_4)_2(H_2O)_2^-$, by an excess of oxalic acid (17). It is known that at moderate acidities the latter is stable (238).

The kinetics of reduction of $Co(C_2O_4)_3^{3-}$ by Fe^{2+} have been studied in detail (35), and the reaction

$$\mathrm{Fe^{2+}} + \mathrm{Co(C_2O_4)_3^{3-}} \rightarrow \mathrm{Fe^{3+}} + \mathrm{Co^{2+}} + 3\mathrm{C_2O_4^{2-}}$$

is found to be first order in each of the reactants. The second-order rate constant at zero ionic strength,

$$k_0 = 1.6 \times 10^{14} \exp(-12{,}600/RT)\ \mathrm{M^{-1}\ min.^{-1}}$$

and the observed kinetic salt effects up to an ionic strength of 0.004 are in agreement with the Brønsted theory (320).

(b) Electrode-potential studies

The effect of complexation on the E^0 value of a couple in the presence of complexing substances in solution is discussed in a recent review (329). Data on the E^0 values of couples involving oxalato complexes are shown in table 17. From a knowledge of the stability constants it is possible to calculate the E^0 value of the metal–oxalato electrode. The E^0 value is thus calculated for the Ag-$AgC_2O_4^-$ electrode from recent data on the stability constant of the complex (see table 11). The lowering of the E^0 value of the Mo^V/Mo^{VI} couple as a result of complex formation in oxalic acid medium has been observed (402).

(c) Electron-exchange reactions

The electron-exchange reactions between the oxalato complexes of a metal in two different oxidation states are of interest in learning about the specific anion effect on the rate of electron-transfer exchange. Exchange between Mn*(II) and Mn(III) has been reported by Polissar (336) in oxalic acid medium to be fast. Subsequent studies by Adamson (6) of the same system in perchloric acid show that the exchange is rapid but measurable ($t_{1/2}$ ca. 10-20 sec.). This suggests that the observed fast exchange between manganese(II) and manganese(III) in oxalic acid medium may well be between the respective oxalato complexes. Similar acceleration of the exchange rate between thallium(I) and thallium(III) was observed in the presence of oxalic acid (61). More extensive studies have been made on the electron-transfer reaction between cobalt(II) oxalato/cobalt(III) oxalato complexes using Co^{60} (7, 99), as well as C^{14} (99), and these have been related to the photochemical and thermal decomposition of $Co(C_2O_4)_3^{3-}$ (7, 88). The mechanism of exchange is not unequivocally established, although the exchange is

TABLE 17

Oxidation potentials of oxalate electrodes

Oxalato Complex	E^0	Metal	E^0	References
	volts		*volts*	
$V(C_2O_4)_{p-2}^{6-2p} + 2C_2O_4^{2-} = V(C_2O_4)_p^{3-2p} + e^-$	0.89 (pH ~4.5)	V^{2+}/V^{3+}	0.25	(261)
$Ti(C_2O_4)_2^- + H_2O = TiO(C_2O_4)_2^{2-} + 2H^+ + e^-$	0.0	Ti^{3+}/TiO^{2+}	(−0.1)	(327)
$Fe(C_2O_4)_2^{2-} + C_2O_4^{2-} = Fe(C_2O_4)_3^{3-} + e^-$	−0.02	Fe^{2+}/Fe^{3+}	−0.77	(367)
$Cu^0 + 2C_2O_4^{2-} = Cu(C_2O_4)_2^{2-} + 2e^-$	−0.04	Cu^0/Cu^{2+}	−0.34	(286)
$Zn^0 + 3C_2O_4^{2-} = Zn(C_2O_4)_3^{4-} + 2e^-$	ca. 1.02	Zn^0/Zn^{2+}	0.76	(243, 251)
$Ag^0 + C_2O_4^{2-} = Ag(C_2O_4)^- + e^-$	−0.56	Ag^0/Ag^+	−0.80	(83)

known to be very slow ($t_{1/2}$ ca. 170 hr. at 50°C.). One author (7) explains both Co* exchange and the thermal decomposition of $Co(C_2O_4)_3^{3-}$ in terms of $C_2O_4^-$ participation.

$$Co(C_2O_4)_3^{3-} \leftrightarrows Co(C_2O_4)_2^{2-} + C_2O_4^-$$

$$Co(C_2O_4)_2^{2-} + C_2O_4^{2-} \leftrightarrows Co(C_2O_4)_3^{4-} \quad \text{(rapid equilibrium)}$$

$$Co(C_2O_4)_3^{3-} + C_2O_4^- \rightarrow Co(C_2O_4)_2^{2-} + C_2O_4^{2-} + 2CO_2$$

The thermal decomposition of $Co(C_2O_4)_3^{3-}$ is represented (88) as

$$2Co(C_2O_4)_3^{3-} \rightarrow 2Co(II) + 5C_2O_4^{2-} + 2CO_2$$

with the initial rate-determining step:

$$Co(C_2O_4)_3^{3-} \rightarrow Co(C_2O_4)_2^{2-} + C_2O_4^-$$

and the $C_2O_4^-$ sustains the chain.

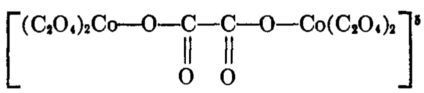
The presence of $C_2O_4^-$ for any finite time in solution is doubted (99) on two grounds: (*1*) exchange between $C_2O_4^-$ and $\overset{*}{C_2}O_4^{2-}$ must be rapid, analogous to a similar system: MnO_4^- and MnO_4^{2-} (384), and (*2*) if exchange is rapid, thermal decomposition should yield C^*O_2. From the absence of any significant radioactivity in the evolved carbon dioxide in experiments on the thermal decomposition of $Co(C_2O_4)_3^{3-}$ in the presence of $\overset{*}{C_2}O_4^{2-}$, it was concluded that the radical-ion, $C_2O_4^-$, does not contribute to the initial decomposition. Instead, the following reaction is proposed as more likely:

$$Co(C_2O_4)_3^{3-} \rightarrow Co(C_2O_4)_2^{2-} + CO_2 + CO_2^-$$

The small activity in the evolved carbon dioxide is explained, therefore, as due to a very slow electron-exchange reaction:

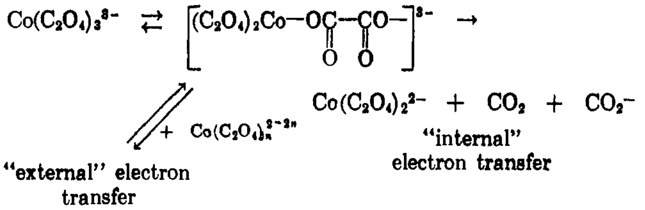
$$Co(C_2O_4)_3^{3-} + Co(\overset{*}{C_2}O_4)_n^{2-2n} \leftrightarrows Co(\overset{*}{C_2}O_4)_3^{3-} + Co(C_2O_4)_n^{2-2n}$$

followed by the decomposition of the active $Co(\overset{*}{C_2}O_4)_3^{3-}$. From the kinetic study of this complicated electron-exchange process, it was deduced that rupture of one of the chelated oxalates as a preliminary step might facilitate electron transfer in the postulated transition state:

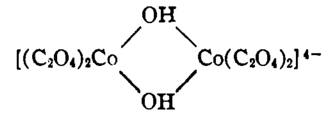


$$\left[(C_2O_4)_2Co{-}O{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}O{-}Co(C_2O_4)_2\right]^{5-}$$

It is interesting to note that traces of cerium(III) catalyzed the exchange (rate constant of uncatalyzed exchange = 2.0×10^{-2} M^{-1} hr.$^{-1}$; rate constant of catalyzed exchange = 8.9×10^{-2} M^{-1}hr.$^{-1}$ at 4×10^{-5} *M* cerium(III) and 17.7×10^{-2} M^{-1} hr.$^{-1}$ at 8×10^{-5} *M* cerium(III)). From these observations the following overall sequence of reactions of $Co(C_2O_4)_3^{3-}$ was proposed (99):



Some inconclusive exchange data for the exchange of Co*(II) in excess oxalate with Durrant's salt



indicate $t_{1/2}$ ~2 hr., and plots of the nonlinear log (1 − fraction exchange) vs. time suggest an induction period (7). These complications are attributed to the general decomposition by acid of Durrant's salt to give the monomeric species, $Co(C_2O_4)_2(H_2O)_2^-$.

6. Thermal decomposition of solid oxalates

There is an extensive literature on the thermal decomposition of what have been called in this review "simple" oxalates. The reactions are all relatively complicated (26) and many products are reported, including carbon, carbon monoxide, carbon dioxide, metal, metal oxides, metal peroxides, and metal suboxides, metal formates, peroxyoxalates, carbonates, and percarbonates. Detailed kinetic studies have been made of only a few compounds: the oxalates of silver(I), mercury(I), mercury (II), nickel(II), and lead(II). In recent years new techniques, particularly that of thermogravimetry, have been applied, and reports have appeared on many bivalent metal oxalates (146, 233, 234, 378, 421), a few rare earth oxalates (70, 433, 434), and two actinide oxalates, thorium(IV) (42, 111, 322), and americium(III) (273). An interesting isotope-effect study has been made of the pyrolysis of lead oxalate (451). Some very early (443) work was concerned with the ignition products of trisoxalatochromium(III) salts. In the presence of air the products were carbon dioxide, chromate, and carbonate. More recently some exploratory work has been done on $K_3Cr(C_2O_4)_3 \cdot 3H_2O$ (432), but no details are given as to decomposition products. Obviously much remains to be done in this area of the chemistry of complex oxalates.

7. Photochemistry: photolysis, actinometry, and photochemical kinetics

The photolysis of oxalate solutions "sensitized" by uranyl salts has been under study for over a century. The use of the reaction for chemical actinometry is well known and has been investigated in great detail (56, 63, 144, 255). The mechanism of the reaction is believed to include the photoactivation of uranyl oxalate complexes, followed by a series of steps involving metastable intermediates, the nature of which may only be surmised

(282). With oxalate in excess, the net reaction is largely decomposition of oxalic acid to carbon dioxide, carbon monoxide, and water, with a minor pH-dependent side reaction leading (in the absence of oxygen) to irreversible formation of uranium(IV). Evidence concerning the kinds of complexes present has been provided by combined photochemical, spectroscopic, and pH-variation studies of uranyl oxalate solution (192). In this work, the species $UO_2H_2C_2O_4^{2+}$, $UO_2C_2O_4^0$, and $UO_2(C_2O_4)_2^{2-}$ were identified, and their (first) dissociation constants at 25°C. were evaluated as 2.7×10^{-3}, 1.5×10^{-6}, and 1.8×10^{-5}, respectively. The latter values agree reasonably well with the figure of 1.2×10^{-5} obtained earlier in a similar study (333). It is of interest that recent flash-photolysis experiments give results which show no marked difference from those obtained in the low-intensity photochemical work and provide confirmation of the existence of relatively long-lived intermediates (325).

Another classic study is that of "Eder's reaction," in which photolysis of a solution containing mercury(II) chloride and an oxalate takes place according to the net reaction:

$$2HgCl_2 + C_2O_4^{2-} \rightarrow Hg_2Cl_2 + 2CO_2 + 2Cl^-$$

The process is very sensitive to inhibitors and catalysts, is markedly dependent on the wavelength of the light employed, and appears to involve a complicated chain mechanism (72, 228). The significant reactant is undoubtedly the complex ion $Hg_2Cl_2(C_2O_4)_2^{2-}$ (76, 78a). The existence of this complex has been recently confirmed in a study of the reaction under the influence of Co^{60} γ-radiation (191). In this case, however, decomposition is not induced by absorption of radiation by the complex. Rather it occurs by a chain of steps promoted by H and OH radicals, which are, of course, always present in aqueous solutions subjected to high-energy radiation.

The photochemistry of solutions of the trisoxalato complexes of chromium(III), iron(III), and cobalt(III) has been repeatedly investigated. Apparently $Cr(C_2O_4)_3^{3-}$ is completely immune to photodecomposition by near ultraviolet or visible light, either at low intensity (9) or under flash-photolysis conditions (325). In contrast, the photoracemization of optically active $Cr(C_2O_4)_3^{3-}$ occurs readily ($\phi = 0.23$) and is essentially independent of wavelength or temperature between 0° and 10°C. (8). The findings conform to the concept of a long-lived doublet state as the photochemical precursor to reaction. The main chemical consequence of the photoactivation is probably breakage of a single Cr—O coördinate bond (see Section III,D,3), for which process the quantum energy even at $\lambda = 700$ mμ should be quite sufficient.

The first significant work on the photochemistry of $Fe(C_2O_4)_3^{3-}$ solutions was that of Allmand and coworkers (13, 14), which has been fully confirmed in later studies (40, 232, 262). It is established that the overall reaction in monochromatic light at room temperature yields, in the absence of oxygen, $FeC_2O_4 + 2CO_2$, with a quantum efficiency of about 0.5. With oxygen present, no ferrous salt appears, and the quantum yield is doubled. A mechanism invoking preliminary photoexcitation of the ferric complex followed by internal electron transfer and dissociation to give ferrous salt and $C_2O_4^-$ or HC_2O_4 radical fits the facts well (324, 325). The oxygen effect is ascribed to direct oxidation of ferrous salt and the radical by molecular oxygen. The existence of the metastable intermediate is supported both by flash-photolysis work (325) and by a proton paramagnetic resonance study (199).

The use of $Fe(C_2O_4)_3^{3-}$ as a chemical actinometer has been strongly recommended and detailed procedures have been developed (41, 190, 323). The method appears to have several advantages over that employing uranyl oxalate, including higher sensitivity, greater stability of photolytic solutions, and simpler analytical technique.

The photolysis of aqueous $Co(C_2O_4)_3^{3-}$ solution has been recently studied in detail (88). The results obtained confirm and supplement earlier work (205, 306, 424). The reaction is similar to that of $Fe(C_2O_4)_3^{3-}$ in regard to its products and in that it appears to involve the reactive radical $C_2O_4^-$. $Co(C_2O_4)_3^{3-}$ differs from $Fe(C_2O_4)_3^{3-}$, however, in that the former undergoes rapid concurrent thermal decomposition (see Section III,D,3). Its rate of photolysis seems to be completely independent of all factors except the rate of light absorption, in agreement with a concept of first-order decomposition of a photoexcited species as the rate-determining process, with no complications of a chain reaction. The lack of oxygen effect in the photolysis of $Co(C_2O_4)_3^{3-}$, as contrasted to that of $Fe(C_2O_4)_3^{3-}$, may be ascribed to the large difference in the Co^{2+}/Co^{3+} and Fe^{2+}/Fe^{3+} oxidation potentials. A further contrast occurs in regard to photoracemization. With $Co(C_2O_4)_3^{3-}$ this is a very inefficient process as compared to photodecomposition (9), while the opposite is true for $Cr(C_2O_4)_3^{3-}$, as discussed above. This is also understandable in terms of difference in oxidation potential, in this case Co^{2+}/Co^{3+} as compared to Cr^{2+}/Cr^{3+}.

Several fragmentary photochemical studies have been made of other oxalato complexes. The rate of decomposition of $Mn(C_2O_4)_3^{3-}$ by polarized and nonpolarized white light has been measured (155). The quantum yield is unity and sulfuric acid inhibits the reaction. A noticeable photochemical "after effect" has also been noted in this reaction (303) and explained in terms of the usual postulate of a metastable intermediate. The photolysis of $K_2Cu(C_2O_4)_2$ requires sensitization by Fe^{3+} or UO_2^{2+}, and the products of decomposition consist of a mixture of metallic copper, copper(I) oxide, copper(II) oxide, carbon monoxide, and carbon dioxide (115). A mechanism consisting of a series of photoactivations and decompositions initiated by the sensitizer has been proposed (46). Photodecomposition of a complex of chloroplatinic acid and oxalate has been reported (31). Finally, some recent work (47) indicates that the bisoxalato complexes of manganese(III), iron(III), cobalt(III), and zinc(II) are photochemically unstable in ultraviolet light, and that $Cu(C_2O_4)_2^{2-}$ and $Ag(C_2O_4)^-$ decompose to give metallic copper and silver under similar conditions. No kinetic data are given.

IV. Applications

A. ANALYTICAL APPLICATIONS

The formation of oxalato complexes has been used in analytical chemistry for the qualitative detection and in some cases for the quantitative determination of metals. The red color of $Mn(C_2O_4)_3^{3-}$ has been recommended for the detection of manganese (264). The photolysis of oxalato complexes of metals known to occur in different oxidation states has also been recommended for developing spot tests (138). One such is the reaction between mercury(II) chloride and $C_2O_4^{2-}$ (Eder's reaction). Photolysis of a mixture of these two reactants, with or without activators such as Fe^{3+} Ce^{4+}, UO_2^{2+} or organic dyes, gives a white precipitate of Hg_2Cl_2, which is used as a spot test for mercury(II) or $C_2O_4^{2-}$. Likewise reduction of H_2SeO_3, iodine, palladium(II) chloride, tungsten(VI) oxide, and methylene blue by oxalic acid is hastened by traces of Fe^{3+} ion and radiation. Photochemical reduction of iron(III) salts by oxalic acid to iron(II) followed by vanadimetric determination has been successfully used for the estimation of iron (158). A new method for the estimation of iodide has been developed using complexing with $Fe(C_2O_4)_3^{3-}$ and catalysis by oxalate ion of the chromium(VI)-iodide reaction (341). The compound $K_3Fe(C_2O_4)_3$ has been used for the detection of cobalt(II) in the presence of nickel(II) as a microscope slide test (355). Inhibition of the precipitation of tin(IV) as the sulfide by oxalic acid has been explained in terms of formation of an oxalato complex of tin(IV) (109).

Separation of niobium(V) and tantalum(V) has been achieved using the oxalato complexes on Dowex-2 columns with the help of Nb^{95} and Ta^{182} as tracers. Although the nature of the oxalato complexes of these elements is not fully understood, it has been possible to elute niobium first, using 1 *M* hydrochloric acid-0.5 *M* oxalic acid as the eluant. Tantalum is later removed with 6 *M* hydrochloric acid (156, 390). An unsuccessful attempt has been made with the help of radiochromatography to utilize the cationic oxalato complexes of iron(II) and cobalt(II) in their separation on the cation exchanger SM-12 (129).

A semiquantitative titration method using methyl red as indicator for the determination of aluminum(III) is reported, in which the formation of several aluminum oxalato complexes is utilized (19). Complexing with oxalate is also useful in effectively masking the precipitation of iron(III), chromium(III), and titanium(IV) in benzoate precipitations of metal ions at varying pH's (400). The microdetection and colorimetric determination of manganese(II) are made by an interesting catalytic reaction involving oxalato complexes of manganese(III). The initial oxidation product of manganese(II) by $Cr_2O_7^{2-}$ in the presence of $C_2O_4^{2-}$ is an oxalato complex of manganese(III), which decomposes at higher temperature (100°C.) to give manganese(II) and carbon dioxide. The newly formed manganese(II) is again oxidized by $Cr_2O_7^{2-}$ to manganese(III) and the cycle continues until all $Cr_2O_7^{2-}$ has been reduced to Cr^{3+}. The resulting green color of the Cr^{3+} ion is an indication of the presence of manganese(II) (15). A method for the determination of calcium(II) or $C_2O_4^{2-}$ by indirect colorimetry has been developed by observing the decrease in optical density when the iron(III)-salicylate complex is treated with oxalate (65). The formation of $Co(C_2O_4)_3^{3-}$, as the basis for a spectrophotometric method, has been employed for the macrodetermination of cobalt. The essential procedure consists in oxidizing all cobalt to cobalt(III) with lead(IV) oxide in the presence of $C_2O_4^{2-}$ and reading the optical density at 600-605 mμ. However, chromium(III), iron(III), calcium(II), manganese(II), nickel(II), and copper(II) interfere seriously with the determination (284, 346). In a new colorimetric procedure for germanium(IV), in which quinalizarin red color is used (absorption peak at 490 mμ), an intermediate step involves extraction of germanium(IV) as $Ge(C_2O_4)_3^{2-}$. The complex apparently responds to this color test (307).

B. INDUSTRIAL APPLICATIONS

The acid properties, reducing action, and chelating ability of oxalic acid and oxalates offer a large number of possibilities for application in industry. Among the many applications of oxalic acid, those involving the formation of metal oxalato complexes occur in tanning, blueprinting, the electrolytic polishing, metal cleaning, or chemical polishing of metal surfaces, electroplating, anodizing, protection against corrosion, ore-dressing, control of soil acidity, polymerization of vinyl compounds, and actinometry. These are further elaborated only in cases where the chemistry of the process is known.

In the chrome tanning process chromium(III)-oxalato complexes find wide application. Recent studies show that the anionic complexes [$Cr(C_2O_4)_2(H_2O)_2^-$ and $Cr(C_2O_4)_3^{3-}$] are more strongly adsorbed by the gelatin gel than the cationic complexes, [$Cr(C_2O_4)$-

$(H_2O)_4^+$ and $Cr(H_2O)_6^{3+}$]. However, experiments on the retention of chromium, using Cr^{51} at pH 4.4–4.6 by the radio- and electrochromatography techniques, indicate that the anionic complexes are first fixed to the collagen and then decompose on the gel phase to become possibly cationic (220, 221, 222).

The chemical reactions in the blueprint process are interpreted in terms of initial photochemical reduction of $Fe(C_2O_4)_3^{3-}$ (302). The solubility of the blue pigments, Prussian and Turnbull's blue, in oxalate media to yield iron(II) and iron(III) oxalato complexes is already known (229, 230).

The auxiliary effect of oxalic acid in the bleaching of indigo by chromium(VI) oxide has been explained in terms of an oxalato complex that can readily supply oxygen for the bleaching observed (399). Oxalic acid as a metal-cleaning agent finds application in removing rust and scales from radiators and other metal surfaces (135, 236, 353, 388). In such chemical polishing processes oxalato complexes are likely to participate in dissolving the oxide coatings on metals (332). Studies of corrosion by oxalic acid on aluminum, iron, copper, tin, and lead are also of interest in view of the complex-forming ability of the metals (450).

Anodizing aluminum in oxalic acid solutions is another interesting application, as is also the technique of electroplating and electropolishing in an oxalic acid bath. The use of oxalato complexes of chromium(III) in chrome plating has been reported (198, 280), and the deposition potential for the oxalato complexes of chromium(III), iron(II), cobalt(II), nickel(II), and copper(II) has been measured (281).

$Mn(C_2O_4)_3^{3-}$ finds application as a catalyst in the polymerization of vinyl compounds (200). The oxalate radical-ion, $C_2O_4^-$, which is known to form in the reaction of potassium permanganate with oxalic acid, as well as in the oxidation of $C_2O_4^{2-}$ by manganese(III), is regarded as the initiator in the polymerization of methyl methacrylate, vinyl acetate, and acrylonitrile.

Simple solid oxalates are industrially important for preparing metal oxides of high purity for powder metallurgy (278) and mixed oxalates as catalysts. For example, the Ni–Mg–C_2O_4 catalyzed hydrogenation of ethyl cinnamate, ethyl butynoate, gaseous benzene, and cyclohexene. Likewise, the catalytic activity of other mixed catalysts, Co–Mg–C_2O_4 and Ni–Zn–C_2O_4, is explained as due to true mixed-crystal formation (249). While simple oxalates are generally prepared by precipitation reactions, at least in the case of $NiC_2O_4 \cdot 2H_2O$, it has been shown that the rate-determining species for nucleation and growth is $Ni(C_2O_4)_2^{2-}$ (11, 12). Turbidimetric and dilatometric kinetics of this precipitation reaction indicate (*1*) self-complexation of Ni^{2+} and (*2*) a heterogeneous reaction on the walls of the vessel.

$$2NiSO_4(aq) + 2H_2C_2O_4(aq) \leftrightarrows Ni(C_2O_4)_2^{2-} \cdot Ni^{2+}(aq) + 2H_2SO_4(aq) \quad (1)$$

$$Ni(C_2O_4)_2^{2-} \cdot Ni^{2+}(aq) \rightarrow 2NiC_2O_4 \cdot 2H_2O(s) \quad (2)$$

Such studies provide data for correlating particle size as a function of precipitating conditions.

Complex formation always has a significant effect on particle size and the latter is important in powder metallurgy. The preparation of powders of pure thorium(IV) oxide of uniform controlled particle size suitable for use as a slurry blanket in a homogeneous reactor has been attempted by the thermolysis of precipitated thorium oxalate and thorium ammonium oxalate. The system $Th(C_2O_4)_2$–$(NH_4)_2C_2O_4$–H_2O therefore has been studied in detail in this connection to learn the effect of complexation on the particle size of the precipitated oxalates (167). Natural bauxite contains iron as impurity, and a method has been developed to treat finely divided ore with oxalic acid at 90–100°C. whereby the oxalato complexes of iron(III) are separated from the insoluble residue containing mostly aluminum. Subsequent photoreduction of the solution in sunlight, followed by evaporation and calcination of iron(II) oxalate, enabled recovery of the iron as pure oxide. The use of $Fe(C_2O_4)_3^{3-}$ in actinometry has already been mentioned; it has the advantage over other actinometers in its simplicity and stability. An interesting use of a digital computer for obtaining the concentrations of the individual chemical species in the iron(III)–oxalic acid system has been reported (401).

C. OTHER APPLICATIONS

Whereas simple oxalates occur in biological systems, complex oxalates do not because the excess oxalate-ion concentration required for the stability of the complexes is toxic. At lower oxalate-ion concentration precipitation results, since the great majority of the simple oxalates are insoluble in water. Simple oxalates are present in low concentration as calcium oxalate in malt and beer (8–20 p.p.m.) (64) and in many other products. Emetic properties have been reported for some oxalato complexes of antimony(III): $HSbC_2O_5$, $KSb(C_2O_4)_2 \cdot H_2O$, $K_2HSb(C_2O_4)_3 \cdot 2H_2O$, $K_3H_2Sb(C_2O_4)_3 \cdot 4H_2O$ (422). A mixture of sodium tungstate and oxalic acid is proposed as a buffer solution for varying pH's, and some complex-ion equilibria are apparently involved in the overall stabilization of pH (45). In a study of the effect of anions on soil acidity some experiments were performed with $C_2O_4^{2-}$. Aluminum in the soil was found to be converted to $Al(C_2O_4)_3^{3-}$, eliminating the often-experienced hydrolytic acidity due to its presence in soil (10). Copper plays an important part in the inhibition of succinic dehydrogenase, and introduction of oxalate into the system causes reversal of this action, presumably owing to complexation and lowering of the copper(II)-ion concentration (196).

The list of applications given here is by no means exhaustive. Many more uses for the oxalates and oxalato complexes can be foreseen, in view of the unique properties of oxalate ion, since it is at once a base, a reducing agent, and a complexing agent.

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