the rate. Such an intermediate might be $[Ni(AA)_2(H_2O)_2]^{+2}$, and it could racemize rapidly in the way suggested for $[Co(en)_2(H_2O)Cl]^{+2}$ by Mathieu.[16] It is also possible that the diaquo $[Ni(AA)_2(H_2O)_2]^{+2}$ is the *trans* isomer and therefore symmetrical. Another possible, but less likely, intermediate would be the tetracovalent and optically inactive $[Ni(AA)_2]^{+2}$.

Formation of the transition state then probably results from expansion of the ion to include two water molecules, resulting in the observed activation energies.[15] This expansion, leading to increased degrees of freedom, also leads to an entropy increase. The entropies calculated for racemization in water at 24.5° are, respectively, 2.6 e.u. for $[Ni(ophen)_3]^{+2}$ and 2.7 e.u. for $[Ni(dipy)_3]^{+2}$.

EVANSTON, ILL.

[16] J. P. Mathieu, *Bull. soc. chim.*, [5] **4**, 687 (1937).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Partial Resolution of the Tris-(oxalato)-germanate(IV) Ion

BY THERALD MOELLER AND NIELS C. NIELSEN

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Preparation and characterization of strychnine and quinine salts of the tris-(oxalato)-germanate(IV) ion have been effected. The covalent nature and octahedral distribution of the bonds in this ion were confirmed chemically by its partial resolution as the quinine salt. The tris-(oxalato)-germanate(IV) ion is an example of a relatively stable "outer orbital" complex involving d-electrons.

Introduction

The orbital hybridization essential to octahedral geometry in 6-coördinate covalent inorganic complex species is most commonly of the type $(n-1)d^2nsnp^3$. Complexes based upon this kind of electron arrangement are often relatively stable with respect to the displacement of one ligand by another and, if asymmetric, are frequently resolvable into optical isomers. Because of the nature of the hybridization, Taube[1] has referred to these materials as "inner orbital" complexes. With cations of elements following the transition series, however, the $(n - 1)$d-orbitals are completely occupied, and any hybridizations in the 6-coördinate complexes must of necessity be of the $ns\ np^3\ nd^2$ type. Since nd-orbitals are inherently more energetic than $(n - 1)$d-orbitals, such "outer orbital" complexes[1] may be expected to be somewhat less covalent in character than the inner orbital species and as a result to undergo more rapid displacement reactions and to be less likely to be resolvable in asymmetric combinations. Such is indeed the case, and many of the reported resolutions of materials of this type must be questioned.[1] Taube points out, however, that as the charge of the metal ion increases, enhanced stability does result.[1]

A case in point is the tris-(oxalato)-germanate(IV) ion. This ion was obtained in solution by reaction of germanium(IV) oxide with either oxalic acid or ammonium hydrogen oxalate[2] but could not be isolated as a simple salt. In solution, it was found to be stable toward hydrogen sulfide, although germanium(IV) sulfide is very insoluble, and to be decomposed only by hot, concentrated sulfuric acid. The stability of the species toward sulfide ion has been used in the processing of germanite as a means of removing other metal ions from germanium.[3] Treatment of the species in solution with solutions of quinine oxalate and strychnine oxalate gives slightly soluble crystalline compounds which were formulated[3,4] $QH_2[Ge(C_2O_4)_3]$ and $(StH)_2[Ge(C_2O_4)_3]$, where Q = quinine, $C_{20}H_{24}O_2N_2$, and St = strychnine, $C_{21}H_{22}O_2N_2$. Infrared data for the species are comparable with those for other oxalato complexes.[5]

The apparent stability of the tris-(oxalato)-germanate(IV) ion and its ability to form salts with optically active bases suggested the feasibility of its resolution through established crystallization and precipitation techniques. This resolution has in fact been accomplished with the quinine compound, providing apparently the first recorded resolution of a 6-coördinate outer orbital complex of a tetrapositive ion. Some comparative X-ray diffraction data have been obtained also.

Experimental

Materials and Apparatus.—The germanium(IV) oxide used was a chemically pure sample obtained from the Indium Corporation of America. Other chemicals were chemically pure reagents and were used without further purification.

All measurements of rotation were made at 30° with a Franz Schmidt and Haensch Polarimeter, using a 2-m. tube and sodium-D light. X-Ray diffraction patterns were taken with a Hayes X-Ray Diffraction unit using cobalt and chromium targets.

Preparation of Alkaloid Salts.—Quinine and strychnine salts of the tris-(oxalato)-germanate(IV) ion were prepared exactly as described previously,[3,4] using 0.35–2.00-g. samples of germanium(IV) oxide. In addition, several samples of the quinine salt (samples 1-1 through 1-4, Table I) were prepared from the parent acid solution by adding quinine in absolute ethanol rather than as oxalate. The compounds were obtained in *ca.* 85% yields, based upon the germanium used, and compared well in properties with those previously described.[3,4] The quinine compound was notably hygroscopic, but the strychnine derivative could be dried and recrystallized. In contrast to the results of Tchakirian,[3,4] analysis showed the presence of two moles of the alkaloid in the quinine derivative.

Anal. Calcd. for $(C_{21}H_{22}O_2N_2 \cdot H)_2[Ge(C_2O_4)_3]$: Ge. 7.21; C, 57.22; H, 4.57; N, 5.56. Found: Ge,[6] 7.40; C, 57.19; H, 4.80; N, 5.46. Calcd. for $(C_{20}H_{24}O_2N_2 \cdot H)_2[Ge(C_2O_4)_3]$: Ge, 7.35; C, 55.95; H, 5.08; N, 5.67. Calcd. for $(C_{20}H_{24}O_2N_2 \cdot H_2)[Ge(C_2O_4)_3]$: Ge, 10.95; C, 47.09; H, 3.92; N, 4.22. Found: Ge, 7.06[6]; C, 57.80; H, 5.75; N, 6.24.

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[1] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[2] J. Bardet and A. Tchakirian, *Compt. rend.*, **189**, 914 (1929).

[3] A. Tchakirian, *Ann. chim.*, [11] **12**, 415 (1939).

[4] A. Tchakirian, *Compt. rend.*, **204**, 356 (1937).

[5] F. Douville, C. Duval and J. Lecomte, *ibid.*, **212**, 697 (1941).

[6] Calculated from GeO_2 residue.

Resolution Studies.—Both fractional crystallization and fractional precipitation techniques were employed.· No resolution was noted under any circumstance with the strychnine compound. With the quinine derivative, however, slow cooling of a solution of the quinine salt with periodic removal of the crystallized product, dissolution of the latter, and examination with the polarimeter gave the data listed under series 1 in Table I. Correspondingly, addition of fractional equivalents of quinine oxalate solution to a solution of the oxalato acid, removal of the precipitates, and treatment of the latter in a similar fashion gave the data listed under series 2 in Table I.

TABLE I

OPTICAL PROPERTIES OF SOLUTIONS OF THE QUININE SALT

Series	Sample	Rotation, deg. Obsd.	Specific, $[\alpha]^{30}_{D}$
1[a]	1-1	−0.40	−200
	1-2	− .31	−152
	1-3	− .28	−140
	1-4	− .20	−100
2[b]	2-1	−1.45	−145
	2-2	−1.21	−121
	2-3	−1.18	−118
	2-4	−1.15	−115

[a] Concentration = 0.100 g./100 ml. [b] Concentration = 0.125 g./100 ml.

Removal of quinine from fractions 1-2, 2-1, and 2-4 was effected by grinding each with slightly more than the calculated quantity of solid potassium iodide and extracting the oxalato germanate(IV) species from the insoluble quinine iodide with water. After dilution of the resulting solutions to the stated concentrations, the rotations given in Table II were obtained. That these fractions contained no quinine was shown by the complete racemization at room temperature of the solution of sample 1-1 in 21 hr. and of solutions of samples 2-1 and 2-4 in 40 hr.

TABLE II

OPTICAL PROPERTIES OF QUININE-FREE SPECIES

Sample	Concn., g./50 ml.	Rotation, deg. Obsd.	Specific, $[\alpha]^{30}_{D}$
1-2	0.0185	−0.06	−81
2-1	.125	− .42	−84
2-4	.125	− .37	−74

X-Ray Diffraction Measurements.—Powder patterns taken for samples of the quinine salt were complicated by the presence of quinine, which gave obscuring halos, and could not be compared exactly with patterns for tris-(oxalato)-cobaltate(III), -chromate(III) and -ferrate(III) compounds. Qualitative similarities, however, and d-spacings of 1.17 and 1.30 Å., as compared with values of 1.14 and 1.27 Å. for potassium tris-(oxalato)-cobaltate (III), do give added support to the presence of the $[Ge(C_2O_4)_3]^=$ ion.

Discussion

The data in Table II indicate clearly that at least a partial resolution of the tris-(oxalato)-germanate(IV) ion has been effected. The nearly identical $[\alpha]^{30}_{D}$ values for the first two samples are in accord with expectation since these two samples represent equivalent fractions in the two series. The lower value for the third sample is in agreement with the general decreases noted in Table I as fractionation proceeded and is probably due to the appearance of an increased quantity of the dextrorotatory form of the complex.

The existence of optical isomerism in the tris-(oxalato)-germanate(IV) ion shows clearly the predominantly covalent character of the bonding involved and suggests the existence of the stable outer orbital hybridization 4s 4p³ 4d². It would be of particular interest to study the exchange between bound oxalate and oxalate ion by Long's technique[7] as a further test of Taube's views.[1]

[7] F. A. Long, THIS JOURNAL, **61**, 570 (1939); **63**, 1353 (1941).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Preparation and Properties of Zirconium and Hafnium Chelates of Certain β-Diketones[1]

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Compounds of zirconium and hafnium with the composition MK_4 have been prepared with the following diketones: acetylacetone, trifluoroacetylacetone, 2-furoylacetone, 2-furoyltrifluoroacetone, 2-thenoylacetone, 2-thenoyltrifluoroacetone and 2-pyrroyltrifluoroacetone. The densities of the chelate compounds were determined by the standard pycnometric method using water or petroleum ether saturated with the chelate as the immersion liquid. The molecular volumes calculated, in all cases, were greater for the hafnium compound than the zirconium compound except for acetylacetone and 2-pyrroyltrifluoroacetone derivatives where the molecular volumes were almost identical. The ultraviolet absorption spectra for the non-fluorine containing chelate compounds in cyclohexane are similar to the parent diketones. For the metal derivatives of the fluorinated diketones, the λ_{max} associated with the enol ring is shifted to longer wave lengths, as compared to the λ_{max} of the free diketone. The λ_{max} for the zirconium chelates shifted to slightly longer wave lengths than for the corresponding hafnium compound.

Although certain diketones have been used for the fractional separation[2] of zirconium and hafnium, little is known about the properties of the solid metal chelates themselves. It was of interest therefore to isolate some of the solid products and examine their properties. Chelates of the following diketones were prepared: acetylacetone (HCCA), trifluoroacetylacetone (HCTA), 2-furoylacetone (HFCA), 2-furoyltrifluoroacetone (HFTA), 2-pyrroyltrifluoroacetone (HPTA), 2-thenoylacetone (HTCA) and 2-thenoyltrifluoroacetone (HTTA). Attempts to synthesize 2-pyrroylacetone were unsuccessful.

Densities, Molecular Volumes.—One of the properties studied was the molecular volume of the solid chelate, since it has been suggested[3] that molecular volume data may shed some light on the

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[1] Based on a thesis submitted by Glenn Terry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, and carried out under Task Order 4 of Contract N7onr-28504 between the Office of Naval Research and the University of Wisconsin. Presented in part at the September 15, 1952, Atlantic City Meeting of the American Chemical Society before the Physical and Inorganic Division.

[2] E. M. Larsen and G. Terry, THIS JOURNAL, **75**, 1560 (1953).

[3] W. Biltz, *Z. anorg. Chem.*, **164**, 245 (1927).