Fig. 1 is −4.5 kcal./mole. Unfortunately, there seem to be no data that would give even approximate values for the $\bar{L}$'s of the positive ions in this medium so that the total contribution to the apparent enthalpy cannot be assessed. Experimentally, we have been unable to measure the temperature dependence of the line broadening at low perchloric acid concentrations, where the $\bar{L}$'s would be expected to be small. It would be necessary to be able to measure much smaller line broadenings than our equipment permits so as to use low manganese concentrations and thus avoid the problems due to change in solubility with temperature. It seems quite possible that in this case the various terms contributing to the temperature coefficient are similar in magnitude and that the over-all effect cannot be simply interpreted.

The argument for an inner-sphere complex requires consideration of the possible origins of the observed broadening. Nuclear electrical quadrupole broadening and the magnetic isotropic hyperfine interaction appear to be the most likely sources. The absence of broadening effects for all ions but Mn^{++} suggests that the quadrupole effects are small. Be^{++} ion was tried because it was thought that quadrupole effects might appear. A rough calculation of the expected quadrupole effect suggests also that the effect would be too small to explain the observed broadenings. It seems significant that Mn^{++} has the longest electron spin relaxation time of all the ions studied (*ca.* 3×10^{-9} sec.).[7,8] It also is well known that Mn^{++} is particularly effective in relaxing nuclear spins. Effects on protons in the case of the hydrated Mn^{++} ion have been explained on the basis of the interaction of electron and nuclear spins,[9] and it seems likely that the perchlorate case is similar. The absence of broadening in the cases of the other ions studied then may be due to the short electron spin relaxation times involved, and complexes cannot be ruled out on the basis of the data obtained here. Since the Mn^{++} ion is separated from the Cl^{35} by at least one oxygen atom it appears that some covalent bonding is involved between the Mn^{++} and ClO_4^- ions. An outer-sphere complex presumably would involve largely ionic hydrogen bonding between the hydrated cation and the perchlorate ion, and, in addition, at least two oxygen atoms and a hydrogen atom would be interposed between the two relevant centers. It seems to us very unlikely that this situation would give rise to any significant broadening of the Cl^{35} absorption line. Therefore, we consider the formation of an inner-sphere complex to be the most probable explanation of our findings. A single experiment using 12 *M* $HClO_4$ saturated with Gd^{3+} (*ca.* 0.05 *M*) showed no broadening detectable with our apparatus. Gd^{3+} has a relatively long electron spin relaxation time but the f electrons are not likely to be involved in the binding even if a ClO_4^- complex exists and thus broadening would not be observed.

The observation of a Mn^{++}–perchlorate complex in perchloric acid appears to be due to a combination of the great effectiveness of Mn^{++} ion in relaxing nuclear spins and the high activity coefficients of perchloric acid. The high activity coefficients probably are related to the relatively small amount of "free water" in the solutions, since the hydrated protons may tie up a considerable amount of water. In the most concentrated solutions there may not be enough water to satisfy both the protons and the manganous ions, and it is conceivable that at least one perchlorate ion might be found in the first coördination sphere of Mn^{++}. The broadening effect persists, however, even in 5 *M* acid where considerably more water is available for hydrating the ions. We feel, therefore, that our results have practical chemical significance for the study of equilibrium and rates in solutions containing perchlorate ions.

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[7] N. Bloembergen and L. O. Morgan, *J. Chem. Phys.*, **34**, 842 (1961).

[8] A. Abragam, "The Principles of Nuclear Magnetism," Oxford Univ. Press, London, 1961, p. 330.

[9] See for example, L. O. Morgan and A. W. Nolle, *J. Chem. Phys.*, **31**, 365 (1959).

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Some New Asymmetric Octahedral Complexes of Arsenic(V)

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The complexes formed with arsenic acid and the four ligands 4-chlorocatechol, 3-methylcatechol, 4-methylcatechol, and 2,3-dihydroxynaphthalene have been prepared, characterized, and resolved. All of these complexes undergo a second-order asymmetric transformation in alcoholic solution in the presence of suitable alkaloids.

The present study was concerned with the preparation, characterization, and resolution of complexes of arsenic acid with *o*-dihydroxy aromatic compounds. Earlier studies of the organic complexes of arsenic(V) have been concerned almost exclusively with the catechol complex. This was prepared by Weinland and Heinzler,[2] resolved by Rosenheim and Plato,[3] and sub-

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[1] To whom correspondence concerning this paper should be addressed.

[2] R. Weinland and J. Heinzler, *Ber.*, **52**, 1316 (1919); **53**, 2765 (1920).

[3] A. Rosenheim and W. Plato, *ibid.*, **58B**, 2000 (1925).

sequently studied by others.[4–7] The complex with 2,3-dihydroxynaphthalene was prepared by Weinland and Seuffert[8] but not examined in detail. The goals of the present work were three in all. The first was to determine if such complexes are inert, the second was to determine if the second-order asymmetric transformation[9] found with the catechol complex of this type is a general process for complexes of this sort, and the third was to determine if such complexes generally contain a molecule of water firmly coördinated to the arsenic as is also characteristic of the catechol complex. A second-order asymmetric transformation has been reported for coördination compounds in only a few instances.[10]

Experimental

The complex acids were prepared by the interaction of solutions of arsenic acid with the dihydroxy compound. The general reaction may be written as

$$H_3AsO_4 + 3RC_6H_3(OH)_2 \longrightarrow H[As(RC_6H_3O_2)_3]\cdot xH_2O + (4 - x)H_2O$$

where R represents a substituent or other group attached to the catechol moiety.

Complex Acid from 2,3-Dihydroxynaphthalene.—The 2,3-dihydroxynaphthalene complex was prepared according to the method given by Weinland and Seuffert.[8] However, in contrast to the five moles of water of hydration found by Weinland and Seuffert, we found two different species existed, the dark tan monohydrate and the white sesquihydrate. An effort was made to determine the amount of water involved in the apparently reversible change of hydration. Samples of the white form of the acid were dried at 1 mm. pressure or less for 4 days in an Abderhalden apparatus containing boiling methanol (65°). Magnesium perchlorate was used as a supplementary desiccant in the vacuum system. A sample of 4.1379 g. lost 0.0731 g., while one weighing 3.6993 g. lost 0.0709 g. This corresponds to a loss of one-half mole of water per mole of parent acid.

From elementary analyses it appears that the white and tan forms are the sesquihydrate and monohydrate, respectively. *Anal.* White forms, calcd. for $H[As(C_{10}H_6O_2)_3]\cdot 1.5\ H_2O$: C, 62.41; H, 3.84; As, 12.98. Found: C, 62.66; H, 4.39; As, 12.90. Tan form, calcd. for $H[As(C_{10}H_6O_2)_3]\cdot H_2O$: C, 63.39; H, 3.72; As, 13.18. Found: C, 63.22; H, 4.62; As, 13.00. The acid is insoluble in water, but readily soluble in acidic or basic solution, in alcohol, and in acetone. It melts with decomposition at 154–155°.

Complex Acid from 3-Methylcatechol.—Arsenic pentoxide (0.05 mole) is dissolved in a mixture of water (15 ml.) and 95% ethanol (15 ml.). This is brought to a boil and 3-methylcatechol (0.3 mole) added. The resulting mixture is filtered and the filtrate allowed to deposit crystals overnight. The yield, after washing with two 15-ml. portions of water, is 73%. The product is light gray. It is soluble in water, acetone, and alcohol, and melts with decomposition at 99°. *Anal.* Calcd. for $H[As(C_7H_6O_2)_3]\cdot 2H_2O$: C, 52.84; H, 4.86; As, 15.69. Found: C, 53.82; H, 5.10; As, 15.52.

Complex Acid from 4-Methylcatechol and 4-Chlorocatechol.—It proved impossible to obtain crystals of the solid complex acids derived from these ligands. It was necessary to use aqueous solutions of the acid in the preparation of the various salts. Solutions of the complex of 4-methylcatechol or 4-chlorocatechol were obtained by dissolving the ligand and arsenic acid in a 3:1 molar ratio in a 50–50 by volume mixture of water and ethanol. The alkaloid salts reported in Table I were prepared from solutions which had been allowed to sit for 3 days. The 80% yield indicates that complexation was complete in that time.

General Method for the Preparation of the Alkaloid and Sodium Salts.—A general method was developed for the rapid preparation of the alkaloid salts of the complex acids which was found to be effective for each of the complex acids except those involving catechol and 3-methylcatechol. The crude acid (0.1 mole) is added to a solution of the alkaloid (0.1 mole) in ethanol and the mixture is heated to reflux for 1 min. The solution is poured, with constant stirring, into distilled water (2 l.) and the precipitate collected on a filter. The precipitates generally are slightly colored upon formation, with the colors almost disappearing when the salts are heated for several hours at 105°. The salts are soluble in acetone, alcohol, and basic aqueous solutions. In general, decomposition occurs at about 215°. Analytical data are given in Table I.

The sodium salts of the optically active anions were prepared by a standard procedure. The alkaloid salt (0.05 mole) was treated with ethanol (200 ml.) and 6 *N* NaOH (15 ml.). The solution was heated gently and water added to replace the evaporated ethanol until 200 ml. of water had been added. The solution was heated almost to boiling and filtered through a preheated filter. The recovered alkaloid was washed carefully with several 10-ml. portions of water. The filtrate then was heated gently until its volume was reduced to 30 ml. Upon cooling, the sodium salt separates from solution. Analytical data are given in Table II.

For the complexes derived from 3-methylcatechol or catechol a complete "resolution" *via* the second-order asymmetric induction cannot be achieved by this same process. The method used for these complexes is the same as that reported earlier for the catechol complex.[3]

Analytical Procedures.—The carbon and hydrogen analyses were done by Galbraith Laboratories, Knoxville, Tennessee. The arsenic analyses presented something of a problem and the best results were found by using the procedure given below.

About 0.5 g. of the complex acid or salt was placed in a 600-ml. beaker and 50 ml. of 6 *N* HNO_3 was added. The mixture was boiled until most of the nitric acid evaporated. Concentrated H_2SO_4 (10 ml.) was added along with 25 ml. of water. The solution then was heated until *all* the nitric acid was expelled.

When the mixture cooled, it was added to 170 ml. of water in a Wiij flask. Solid potassium iodide (2 g.) was added and the solution allowed to stand for about 1 hr. in the stoppered flask. Starch then was added as indicator and the solution titrated with 0.1 *N* thiosulfate.

The procedure presented above was developed in the course of this work. It was later discovered that it is similar to the method used by Khaletskii and Gershentsvit,[6] the major difference being our use of nitric acid in the first step of the analysis.

Second-Order Asymmetric Transformations.—To check the occurrence of this phenomenon in these complexes, the reaction between the complex and alkaloids was examined with the complex present in excess. A solution of 0.01 mole of the complex in 100 ml. of 95% ethanol was treated with 0.005 mole of either cinchonine (1.47 g.) or quinine (1.62 g.). The mixture was refluxed for 30 min. and cooled in an ice bath. The precipitated diastereoisomer was filtered out, and the rotation of the filtrate was observed. Data on the sodium salts prepared from the filtrates are summarized in Table III.

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(5) F. G. Mann and J. Watson, *J. Chem. Soc.*, 505 (1947).

(6) A. M. Khaletskii and R. S. Gershentsvit, *J. Gen. Chem. USSR*, **17**, 2066 (1947).

(7) J. H. Craddock and M. M. Jones, *J. Am. Chem. Soc.*, **83**, 2839 (1961).

(8) R. Weinland and H. Seuffert, *Arch. Pharm.*, **266**, 455 (1928).

(9) This term, due to R. Kuhn, *Ber.*, **65**, 50 (1932), is used here with the meaning that it designates a process in which a racemic mixture, in homogeneous solution, interacts with an added asymmetric compound to produce a solid diastereoisomer of *one* of the enantiomorphic forms of the initial racemate in an amount appreciably greater than would be formed if no interconversion of enantiomers were possible.

(10) (a) P. Ray and N. Dutt, *J. Indian Chem. Soc.*, **18**, 289 (1941); **20**, 81 (1943); (b) A. Werner, *Ber.*, **45**, 3061 (1912); (c) D. H. Busch, *J. Am. Chem. Soc.*, **77**, 2747 (1955); (d) F. Basolo lists some additional examples in J. C. Bailar, Jr., "Chemistry of the Coördination Compounds," Reinhold Publishing Co., New York, N. Y., 1956, p. 334.

TABLE I

ALKALOID SALTS OF THE ARSENIC(V) COMPLEXES

Ligand of acid taken	Color	% yield	M.p., °C.	$[\alpha]^{30}_{D}$ [a]	Analysis % C	Analysis % H	Analysis % As	
Cinchonine salts								
2,3-Dihydroxynaphthalene	White	92	188	49°	69.75	4.78	8.88	Theory
					69.86	5.10	8.78	Found
3-Methylcatechol	Gray	50	184	−194°	65.30	5.48	10.18	Theory
					65.05	5.86	10.10	Found
4-Methylcatechol	Yellow	78	...	49°	62.24	5.74	9.70	Theory
					61.61	5.75	9.32	Found
4-Chlorocatechol	Yellow-green	86	...	41°	53.35	4.24	8.99	Theory
					53.67	4.37	8.81	Found
Quinine salts								
2,3-Dihydroxynaphthalene	White	96	198	−46°	67.34	4.97	8.40	Theory
					66.87	4.96	8.62	Found
3-Methylcatechol	Gray	93	...	−215°	64.31	5.53	9.78	Theory
					63.31	5.56	9.48	Found
4-Methylcatechol	Yellow	77	...	−54°	60.07	5.90	9.16	Theory
					59.84	5.17	9.28	Found
4-Chlorocatechol	Yellow-green	88	...	−40°	51.80	4.46	8.51	Theory
					51.59	4.42	8.90	Found

[a] Rotations observed in acetone.

TABLE II

SODIUM SALTS OF THE ARSENIC(V) COMPLEXES

Ligand	Composition	% yield	$[\alpha]^{30}_{D}$ [a]	Analysis % C	Analysis % H	Analysis % As	
$l(-)$ form							
2,3-Dihydroxynaphthalene	$Na[As(C_{10}H_6O_2)_3]\cdot 7H_2O$	46	−20°	51.59	4.62	10.72	Theory
				51.49	4.14	10.81	Found
4-Methylcatechol	$Na[As(C_7H_6O_2)_3]\cdot 1H_2O$	50	−26°	52.29	4.20	15.52	Theory
				51.86	4.64	15.65	Found
4-Chlorocatechol	$Na[As(C_6H_3O_2Cl)_3]\cdot 5H_2O$	38	−21°	35.12	3.11	12.12	Theory
				35.21	3.02	12.68	Found
3-Methylcatechol	$Na[As(C_7H_6O_2)_3]\cdot 2H_2O$	56	−385°	50.44	4.43	14.98	Theory
				50.02	4.56	15.01	Found
$d(+)$ form							
2,3-Dihydroxynaphthalene[b]	$Na[As(C_{10}H_6O_2)_3]\cdot 7H_2O$	39	19°	51.59	4.62	10.72	Theory
				51.12	3.39	9.99	Found
4-Methylcatechol	$Na[As(C_7H_6O_2)_3]\cdot 2H_2O$	49	32°	50.42	4.43	14.97	Theory
				50.96	4.48	15.08	Found
4-Chlorocatechol[b]	$Na[As(C_6H_3O_2Cl)_3]\cdot 5H_2O$	44	22°	35.12	3.11	12.12	Theory
				34.50	5.38	12.60	Found
3-Methylcatechol	$Na[As(C_7H_6O_2)_3]\cdot 2H_2O$	55	395°	50.42	4.43	14.97	Theory
				49.63	4.63	15.00	Found

[a] Rotations observed in water. [b] The $d(+)$ sodium salts, in general, were much more difficult to obtain in a pure form than were the corresponding $l(-)$ salts. We were unable to obtain good samples for these two salts.

Aside from differences due to the different solubilities in the ethanol solutions, two items are apparent. First, rotations of the sodium salts prepared from the diastereoisomers are essentially equal in magnitude but opposite in sign for the quinine and cinchonine salts. Second, the sodium salts prepared from the solutions have rotations which are *very* small and which may be due to contamination with traces of the alkaloids. This is consistent with two mechanisms for the transformation. The first is one in which the alkaloid allows a rapid interconversion of the enantiomorphic forms in solution, with one being continuously removed by the precipitation of one of the diastereoisomers. The second would involve the precipitation of a mixture of the anions by the alkaloid with a subsequent rapid transformation of the mixture into one preferred form whose stability was especially favored by the way in which the crystal was built up. While these transformations may involve configurational activity it seems that they are intimately connected with the formation of a *solid phase* where interactions of a very specific sort may arise from the close approach of the anion to the alkaloid. The present results and the previous study[11] of the hydrolysis of the *d* and *l* forms of the catechol complex are in accord with the study of similar phenomena in organic chemistry where it is found that non-ionizing solvents are media far more conducive to the occurrence of such phenomena than water.[12]

Discussion

From the present study it may be concluded that the asymmetric octahedral complexes of arsenic(V) show certain common features. One of these is the presence of tightly bound water which seems to be present in all but two of the complex salts prepared in the present study. The most satisfactory present picture of these

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(11) J. H. Craddock and M. M. Jones, *J. Am. Chem. Soc.*, **84**, 1098 (1962).

(12) E. E. Turner and M. M. Harris, *Quart. Rev.* (London), **1**, 300 (1948).

TABLE III

OPTICAL ROTATION DATA FOR THE SECOND-ORDER ASYMMETRIC TRANSFORMATION OBSERVED IN A 1-DM. TUBE

	Ligand species			
Source of sample	2,3-Dihydroxy-naphthalene	3-Methyl-catechol	4-Methyl-catechol	4-Chloro-catechol
Cinchonine salt solution	0.05°	−2.40°	0.50°	0.40°
Sodium salt from above solution	−0.01°	−0.04°	−0.02°	−0.02°
Quinine salt solution	−2.25°	−2.65°	−0.40°	−0.30°
Sodium salt from above solution	0.04°	0.03°	0.03°	0.03°

complex anions involves a structure suggested by examination of that proposed for a rather similar rhodium complex.[13] The water is regarded as coördinated to the central atom through oxygen but also is hydrogen bonded to the hydroxyl groups of one of the catechol groups which is otherwise free. One of the hydrogens then can act as the acidic hydrogen and yet the unchelated phenol will be held firmly enough to allow a stable asymmetric structure to exist. Under favorable circumstances this water can be removed to give the simple tris complex without destruction of the compound.

Another obvious feature is that these complex anions all possess a considerable degree of inertness and are all resistant to the attack of hydroxide ion. The final feature is the common occurrence of a second-order asymmetric transformation in the presence of suitable alkaloids. This is the only group of generically related complexes which has yet been shown to behave in this fashion. This would seem to be a characteristic reaction for octahedral complexes of arsenic(V) with 1,2-diphenols. Within this class the ease with which this inversion occurs varies noticeably, but for each complex ion such a process is indisputable. From the separation experiments reported here, the inversion seems to occur at a slower rate with the complexes containing catechol or 3-methylcatechol than with those involving other ligands. The fact that such effects are demonstrably greater in non-ionizing solvents implies that the chief reason for the paucity of inorganic examples of this phenomenon is the common use of water as the solvent in the resolution of complexes.

Acknowledgment.—We wish to thank Dr. A. W. Ingersoll for his comments on these results. This work has been supported by a grant from the U. S. Atomic Energy Commission for which we wish to express our gratitude.

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[13] A. L. Porte, H. S. Gutowsky, and G. M. Harris, *J. Chem. Phys.*, **34**, 66 (1961).

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Reaction of the Uranyl Ion with Amino Acids. Bidentate Carboxylate Chelation[1]

BY ISAAC FELDMAN AND LARYSA KOVAL

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The stability constants determined by the pH method for 1:1 complexes of the uranyl ion with acetate, acid succinate, aspartate, and glutamate ions in acid solution at 25° and $\mu \cong 0.2$ all have practically the same value, log K_1 between 2.61 and 2.70. These results are interpreted as being due primarily to the fact that in each case complexing involves only bidentate carboxylate chelation, which produces significantly less steric hindrance than is present in either uncomplexed, hydrated uranyl ion or in other possible chelate structures. The concept of bidentate acetate chelation of the uranyl ion also is used to explain the apparent anomaly that pK_1 for the uranyl-acetate complex is as high as pK_1 for the uranyl–glycolate chelate. Precipitation studies from pH 3 to 8 indicate that both carboxyl and imidazole nitrogens probably are involved in protein binding of the uranyl ion, but that binding by α-amino groups is insignificant, probably for steric reasons.

Some time ago, Dounce and Lan concluded from qualitative titration and precipitation studies that the uranyl ion is bound to proteins almost exclusively by carboxyl groups.[2]

On the other hand, Li, *et al.*, have concluded that the binding sites of histidine toward the uranyl ion are the amino group and the 'pyridine' nitrogen of the imidazole group.[3] Their pH titration results gave no evidence for complexing of the uranyl ion by glycine, serine, or other α-amino acids in the pH region 3 to 4.3, but from solvent extraction experiments they obtained formation constants of 27 and 7.4, respectively, for glycine and serine complexes near pH 2.[4,5]

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester Atomic Energy Project, Rochester, New York. Presented at the 7th International Conference on Coördination Chemistry at Stockholm, Sweden, 1962.

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