made to identify the powder, which was present in only a very small amount. The solid was removed on a filter and the filtrate was concentrated under vacuum to 50 ml., yielding a red solid. The solid was collected on a filter and the filtrate cooled to −78°, yielding more of the red solid. This was again collected and the filtrate discarded. The two crops of solid were combined and recrystallized from ether; yield 1.2 g. (94%).

Anal. Calcd. for $C_6H_5CSSMn(CO)_4$: C, 41.4; H, 1.57; S, 20.1. Found: C, 41.4; H, 1.83; S, 19.0. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill. They suggest it is difficult to get good results for S in the presence of Mn.

Molecular Weight Determination.—The molecular weight of $C_6H_5CSSMn(CO)_4$ was determined by the isopiestic method.[5] Chloroform solutions of 0.0044 g. of $Mn(CO)_5Br$ and 0.0064 g. of $C_6H_5CSSMn(CO)_4$ equilibrated in a $CHCl_3$ atmosphere at 25° in the dark in 6 days with respective volumes of 0.760 and 0.602 ml. Mol. wt. calcd. for monomer, 320; found, 350.

Spectra.—The infrared spectrum was measured on a Beckman IR-9 in $CHCl_3$. In the carbonyl region bands were found at 2092 (s), 1918 (vs), 1906 (sh), and 1964 (s) cm.$^{-1}$. The visible and ultraviolet spectra were taken on a Beckman DK-2 in benzene (visible) and methanol (ultraviolet). Very intense bands were found at 4060 Å. (ϵ 6900) and 2970 Å. (ϵ 21,500).

Reaction with Methanol.—It was observed that when 0.0269 g. of $C_6H_5CSSMn(CO)_4$ was suspended in 50 ml. of methanol and refluxed for 3 days the color changed from red to yellow. Removal of the methanol by vacuum left a solid. The solid was dissolved in ether and transferred to the base of a sublimation tube. The ether was evaporated in a nitrogen stream and the solid vacuum sublimed at room temperature and 0.5 mm. pressure. The yellow sublimate was washed with ether into a weighed flask and the ether removed in a nitrogen stream followed by drying under reduced pressure. The solid product weighed 0.0137 g. and the infrared spectrum confirmed that it was $Mn_2(CO)_{10}$. Thus 83.4% of the Mn was changed from $C_6H_5CSSMn(CO)_4$ to $Mn_2(CO)_{10}$.

Results and Discussion

The mild reaction conditions and good yield of the reaction

$$C_6H_5CSSH + Mn(CO)_5Br \longrightarrow C_6H_5CSSMn(CO)_4 + CO + HBr$$

must be contrasted with the fact that under identical conditions there was no reaction if C_6H_5COOH was used. Further, upon refluxing an ether solution of benzoic acid and $Mn(CO)_5Br$ for 24 hr. the only carbonyl product obtained was shown by its infrared spectrum to be $[Mn(CO)_4Br]_2$.[4] It was also found that dithiobenzoic acid will not cleave this dimer in boiling ether.

The attempted synthesis of an iron analog by the reaction between C_6H_5CSSH and $Fe(CO)_4Br_2$ in ether under the same conditions was rewarded only by vigorous bubbling and a color change from red to yellow, but immediately the yellow product decomposed to $Fe_3(CO)_{12}$. No method was found to be rapid enough to afford the separation of this yellow product from its decomposition products. However, the infrared spectrum in chloroform taken during the reaction, on a Baird-Associates 4-55, shows the production of three new bands: 2110 (s), 2060 (s), and 2045 (m) cm.$^{-1}$.

The conversion of $C_6H_5CSSMn(CO)_4$ to $Mn_2(CO)_{10}$ in methanol is interesting in regard to its 83% yield. Because the CO:Mn ratio changes from 4:1 in the reactant to 5:1 in the product the maximum expected yield should only be 80%. Thus an experimental yield on the order of 80% must mean that either the carbon monoxide is quantitatively transferred from one molecule of reactant to four other molecules of reactant in boiling methanol or that the methanol is a source of carbon monoxide. In view of the improbability of the first path the decomposition is postulated as the second; as a reaction with the methanol. Refluxing a hexane solution of the material led to the formation of a tar containing only small amounts of $Mn_2(CO)_{10}$. Transfers of a CO from an alcohol to a metal are already known[6] but it appears that this is the first example involving a member of the first row transition series as well as one resulting in a simple metal carbonyl.

The very intense absorption of $C_6H_5CSSMn(CO)_4$ at 4060 Å. (ϵ 6900) is in contrast to the weaker bands found for other disubstituted tetracarbonylmanganese(I) compounds. The λ_{max} for the series $Mn(CO)_4LBr$ where L = CO, $(C_6H_5)_3P$, $(C_6H_5)_3As$, $(C_6H_5)_3Sb$, and $(C_6H_5O_3)P$ are all in the range 3820–4090 Å. but the molar extinctions range from 340 to 730.[7] Dithiobenzoic acid itself has an intense ultraviolet spectrum, the edge of which extends into the visible region but at 4000 Å. ϵ is only 68. A simple explanation of this phenomenon can be based on the direct involvement of the metal in the aromatic system through π-bonding between the metal and the sulfurs. Coupling a cyclic conjugated system like this to the aromatic ring would be expected to enhance both the stability and the absorption of the compound.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Complexes of the Lanthanide Elements with Kojate and Acetylacetonate Ions

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Kojic acid (I) and acetylacetone have been shown to be good chelating agents for a large number of metal ions. There are several publications[1,2] describing the preparation of some kojate complexes and a few concern-

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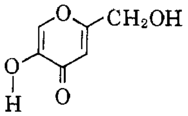
ing the determination of their stability constants.[3,4] A systematic investigation of the formation constants of the lanthanide complexes, however, has not been reported. The formation constants for the acetylacetonate complexes in an aqueous solution of 0.1 *M* ionic strength have been reported by Grenthe and Fernelius.[5]



Kojic acid (I)

The present paper reports the stability constants for the lanthanide complexes of both the kojate and acetylacetonate anions, measured in an aqueous perchlorate solution of 2.0 *M* ionic strength. This ionic strength was chosen to conform with previous investigations from this laboratory.[6,7] The aim of this research was to determine how the stability of the complex is affected by the gradual change in the radius of the cation and by the size of the chelate.

Experimental

Reagents and Equipment.—Lanthanide perchlorate solutions were prepared as described previously.[6] Sodium perchlorate (G. F. Smith Co., anhydrous reagent grade) was used to adjust the solutions to 2.0 *M* ionic strength. Kojic acid (Pfizer and Co.) was purified by the method of McBryde and Atkinson[8] and the buffer solution was prepared by partially neutralizing a standard kojic acid solution with sodium hydroxide, so that the buffer ratio was unity. The acetylacetone (Eastman Organic Chemical) buffer solution was prepared similarly to the kojic acid buffer.

A Beckman Model G pH meter was used with a Beckman Type 42 glass electrode and a silver–silver chloride reference electrode.

Procedure.—The method of Bjerrum, as described in previous publications from this laboratory,[6,7] was used to evaluate first (K_1) and second (K_2) stability constants. The experimental procedure involved titration with the buffer of two solutions of equal ionic strength, the one containing the lanthanide ion and made up to 2.0 *M* ionic strength with $NaClO_4$ and the other containing only $NaClO_4$. The solution to be titrated was placed in a jacketed cell through which water at 25 ± 0.1° was circulated. Nitrogen gas was passed over the solution during the titration. From the pH values recorded after each addition of buffer solution, the concentration of the free ligand, [L], and the average number of ligands bound to metal, $\bar{n}$, were calculated. It is justifiable to use the hydrogen ion activities measured by the pH meter to calculate our "concentration" stability constants since the activity coefficients of the hydrogen ion cancel out in the calculation of [L].[6] A summary of the results of the titrations is given in Table I. Only those values of $\bar{n}$ and [L] which describe the formation of the first and second complexes were used with an IBM-709 program based on a graphical method for evaluation of K_1 and K_2.[9] All the data were used in a second program[10] to calculate very approximate values of log K_3. These ranged about 3.5 for both ligands.

TABLE I

SUMMARY OF RESULTS

Metal ion	Total metal concn., m*M*	pH range	No. of data points	Maximum $\bar{n}$ attained
		Kojate		
La	2.246	4.70–7.29	15	2.41
Pr	1.636	5.09–7.32	13	2.41
Sm	2.329	4.62–7.17	15	3.21
Eu	2.165	4.86–7.18	14	2.90
Gd	2.251	4.80–7.10	14	3.21
Dy	2.458	4.38–6.95	14	3.50
Er	2.371	4.30–7.10	15	3.56
Tm	2.427	3.79–7.10	16	3.97
Lu	2.287	3.58–7.13	15	3.52
Y	2.545	4.48–7.10	16	3.81
		Acetylacetonate		
La	2.246	6.42–8.02	10	1.59
Pr	1.636	6.75–7.95	8	1.76
Sm	2.329	6.27–7.58	11	2.05
Eu	2.165	6.29–7.79	11	2.15
Gd	2.251	6.23–7.87	12	2.45
Dy	2.458	5.89–7.61	12	2.33
Er	2.371	5.97–7.83	12	2.42
Tm	2.427	5.35–7.49	12	2.34
Lu	2.287	4.78–7.42	9	3.29
Y	2.545	6.05–7.30	11	1.91

TABLE II

STABILITY CONSTANTS

25° and 2.00 *M* ionic strength

Metal ion	Kojate		Acetylacetonate	
	log K_1	log K_2	log K_1	log K_2
La	5.14	4.13	4.71	3.45
Pr	5.18	4.58	5.01	3.83
Sm	5.38	5.20	5.32	4.40
Eu	5.35	5.10	5.41	4.30
Gd	5.49	5.17	5.42	4.39
Dy	5.74	5.39	5.74	4.48
Er	5.72	5.60	5.70	4.38
Tm	6.00	5.55	6.03	4.72
Lu	6.24	5.60	5.98	4.78
Y	5.43	5.38	5.57	4.59

Results and Discussion

Table II lists the values of the stability constants K_1 and K_2 calculated from the $\bar{n}$ and [L] values. Error limits were estimated from maximum and minimum values of $\bar{n}$ and [L] obtained by variation within the determinate error of the experimental data. By this procedure, the error limits were found to be ±10% for K_1 and ±20% for K_2.

In a comparison of the stability constants of Mg(II) and Mn(II) complexes, Murakami concluded that the kojate complexes were stronger than the acetylacetonate complexes.[4] He ascribed this to the greater basicity of the enol group of the acetylacetonate ligand and to the resonance stabilization of the heterocyclic chelate ring of the acetylacetonate complexes. However, the difference was very small for Mn(II) and, considering the differences in ionic strength, it would seem better to conclude that for this metal ion the kojate and acetylacetonate complexes have similar stability. For the few other metal ions studied with both ligands,[11] dif-

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ferences in solvent media and in ionic strength make comparisons questionable. However, on a qualitative basis it would seem that in a common system only Mg(II) has greater stability with acetylacetonate. Cd(II) and Zn(II) show greater stability for kojate, while the acetylacetonates and kojates of Co(II), Mn(II), Ni(II), and Cu(II) have relatively similar stabilities.

The lanthanide ions also show similar stabilities for these two ligands. This suggests that the increased stability of the five-membered ring formed by kojate complexing balances the expected stabilization of the acetylacetonate complexes due to the resonance in the chelate ring and to the greater basicity of this ligand. More detailed discussion of the relative complexing of these two ligands as well as of the more subtle question of the differences of the stability of the complexes as a function of atomic number of the lanthanide ions is not possible with free energy data alone.

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Some Reactions of Oxygen Difluoride

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As a part of a program of investigation of reactions of compounds containing the O–F group, a study has been made of reactions of oxygen difluoride, OF_2. The results are presented briefly here, but are given at length in a source available to all.[1]

One generalization which should be emphasized is that oxygen difluoride forms violently explosive mixtures with many substances.

Experimental

Basic Hydrolysis of Oxygen Difluoride.—Oxygen difluoride is known to react with dilute solutions of sodium hydroxide at about 0° and above to give oxygen and fluoride ion. If hypofluorite ion is formed, it decomposes rapidly giving oxygen. Since a low temperature should favor a low rate of decomposition, an attempt (which proved to be unsuccessful) was made to obtain hypofluorite ion by contacting oxygen difluoride with 40% KOH solution at −45° while stirring the liquid. Under these conditions the rate of production of oxygen was very low indeed, but the rate of absorption of oxygen difluoride, after saturation of the solution with OF_2, was also very low. If hypofluorite ion had been formed, oxygen fluoride should have dissolved rapidly and in large amount. The low rate of basic hydrolysis suggested the possibility that oxygen difluoride might be produced in high yield by the reaction of fluorine with 40% potassium hydroxide at −45°. This proved not to be the case. Yields about 9% of theoretical were obtained.

The reaction $OF_2 + 2\,OH^- \rightarrow H_2O + O_2 + 2F^-$ is known to be first order with respect to OF_2.[2] First-order rate constants were determined for the hydrolysis of oxygen difluoride in 40% potassium hydroxide while shaking the system, with the results shown in Table I.

TABLE I

HYDROLYSIS OF OF_2 IN 40% KOH

	248°K.	273°K.	293°K.
k (sec.$^{-1}$) for $-d(OF_2)/dt = k(OF_2)$	2.8×10^{-4}	9.5×10^{-4}	2.2×10^{-3}

Reaction of Oxygen Difluoride with Halogens.—Ruff and Menzel[3] found ClF to be a product of the reaction of OF_2 with **chlorine.** In the present work, a mixture of equal volumes of chlorine and oxygen difluoride exploded upon ignition by a spark to give ClF and oxygen.

When a mixture of three volumes of OF_2 with one of $\mathbf{Br_2}$ vapor was ignited by heat or a spark, oxygen was formed together with much BrF_3. By exploding a 5:1 mixture of OF_2 with Br_2, bromine pentafluoride was formed together with oxygen.

Iodine was found to react slowly at room temperature with oxygen difluoride to give iodine pentafluoride and a yellow solid. Numerous runs using a variety of procedures gave solids of various compositions IO_xF_y shown in Table II.

TABLE II

OBSERVED COMPOSITIONS OF IO_xF_y

Formed by reaction of I_2 in CCl_4 soln. with OF_2 gas		Formed by reaction of I_2 vapor with OF_2 gas	
x	y	x	y
0.78	1.43	0.96	1.61
0.66	1.43	1.07	1.48
0.80	1.68	1.01	1.49
0.83	1.58	1.98	0.37
1.31	1.31	1.79	0.35
		1.81	0.40

The yellow solid was substantially insoluble in liquid sulfur dioxide, trifluoroacetic acid, trifluoroacetic anhydride, or carbon tetrachloride. It reacted with water or hydrogen fluoride. No way was found to separate the solid into its components by the use of solvents.

At an elevated temperature iodine burned in oxygen difluoride, forming iodine pentafluoride and oxygen.

Iodine chloride, ICl, vapor reacted readily at room temperature with oxygen difluoride forming a yellow-orange smoke which settled out as a solid having the composition $IO_xF_yCl_z$ in which x, y, and z had the values indicated in Table III for various runs. The solid must have been a mixture. As in the case of the product from iodine, it was not found possible to separate the mixture into pure substances by using solvents.

TABLE III

PRODUCT FROM REACTION OF ICl WITH OF_2

x	y	z
1.16	1.49	0.54
0.82	1.20	1.21
1.38	0.52	0.87
1.32	0.90	0.17

Reaction with Sodium Thiocyanate.—Ruff and Menzel[3] found that OF_2 reacted with a solution of potassium thiocyanate to give a brick-red precipitate and other products. In this research as a stream of oxygen difluoride diluted with nitrogen was

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[1] Thesis of Robert A. Rhein, Order No. 63-4440, University Microfilms, Ann Arbor, Mich., 60 pp., microfilm copy $2.75, xerography copy $3.00, 1963.

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