

COMMUNICATIONS TO THE EDITOR

CHELATION OF THE +3 IONS OF ELEMENTS
95 THROUGH 100 WITH THENOYLTRIFLUORO-
ACETONE

Sir:

Certain reaction properties of the +3 aqueous ions of members of the lanthanide and actinide series of elements appear to correlate with the contraction in ionic radii observed in crystals with increasing atomic number. The usual order of elution by complexing agents from ion exchange columns, namely, in order of decreasing Z , is thus said to be the result of the variation in basicity or charge separation.^{1,2}

We have observed some remarkable variations in the extraction equilibria of the thenoyltrifluoroacetates of the +3 actinides in toluene-aqueous systems (Table I). All equilibrations were conducted to obtain relative extractabilities, *i.e.*, at least two of the elements were present in each of the numerous systems studied to determine the distribution ratios. Trace concentrations of the nuclides Ac²²⁵, Am²⁴¹, Cm²⁴⁴, Bk²⁴⁹, Cf²⁵², 99²⁵³ and 100²⁵⁴ were available for the measurements. Radioactive properties of the newer nuclides have been given in recent publications.^{3,4}

TABLE I

DISTRIBUTION RATIOS OF ACTINIDE AND LANTHANIDE IONS

Element	D^a	Element	D^a
Europium	0.82	Berkelium	4.15
Ytterbium	5.59	Californium	2.20
Actinium	0.0001	99	1.60
Americium	.29	100	2.58
Curium	.24		

^a Concentration ratios (toluene/aqueous, volume basis) at equilibrium in the distribution of the +3 ions between 0.2 M thenoyltrifluoroacetone in toluene and 0.088 M ammonium monochloroacetate buffer solution, pH 3.4, *ca.* 25°.

Equilibrium concentrations in the two phases were determined by α - and β -particle counting, spontaneous fission counting, and α -particle pulse analysis. With the exception of element 100, the dependence of the extraction on acid concentration has been measured for all these elements and found to be inversely proportional to the third power of the acid concentration. These experiments give direct evidence that the stable oxidation state of the new elements berkelium, californium and element 99 is, indeed, the +3 state. The distribution ratios of Table I were determined with the aqueous phase buffered with ammonium monochloroacetate. Other equilibrations of Eu,

(1) E. R. Thompkins, J. X. Khym and W. E. Cohn, *THIS JOURNAL*, **69**, 2769 (1947).

(2) S. G. Thompson, B. B. Cunningham and G. T. Seaborg, *ibid.*, **72**, 2798 (1950).

(3) P. R. Fields, M. H. Studier, J. F. Mech, H. Diamond, A. M. Friedman, L. B. Magnusson and J. R. Huizenga, *Phys. Rev.*, **94**, 209 (1954).

(4) H. Diamond, L. B. Magnusson, J. F. Mech, C. M. Stevens, A. M. Friedman, M. H. Studier, P. R. Fields and J. R. Huizenga, *ibid.*, **94**, 1083 (1954).

Am, Cm, Cf and 99 indicate that the +3 states exist as complex ions with one chloroacetate ion per metal ion. The order of extractability appears to be independent of the aqueous phase complexing.

A change in behavior noted in ion exchange studies at the expected position for half-filling of the 5f electron shell is attributed to a discontinuity in ion size.² The distribution ratios of Table I also show an abrupt change between Cm and Bk. The distributions in general, however, do not conform to any simple size dependent pattern which might have been anticipated from the trends in crystal radii of these ions.

Radioactive traces of europium and ytterbium were present in a few of the equilibrations, but a general comparison of the properties of the lanthanides and actinides must await adequate thermal data. The comparative study of the two series in this system should be particularly effective for the examination of aqueous phase complexing, polarizability, bonding strengths, and entropy effects.

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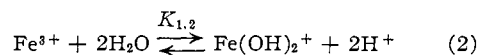
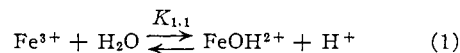
M. L. ANDERSON

RECEIVED OCTOBER 23, 1954

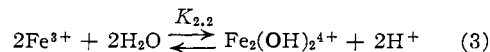
THE HYDROLYSIS OF Fe³⁺ ION: MAGNETIC AND
SPECTROPHOTOMETRIC STUDIES ON FERRIC
PERCHLORATE SOLUTIONS

Sir:

Several workers^{1,2} have studied the hydrolysis of Fe³⁺, or the association of this ion with other ions, employing generally electrochemical or spectrophotometric methods. Most of these workers have considered the following types of equilibria for the study of hydrolysis:



Recently Hedström³ proposed another equilibrium



and from e.m.f. measurements obtained values for the equilibrium constants $K_{1,1}$, $K_{1,2}$, and $K_{2,2}$ at 25°.

From measurements of magnetic susceptibility, over a range of temperature, of 0.04 M ferric perchlorate, 3 M sodium perchlorate, aqueous solutions of varying acidity, we have found that the species $\text{Fe}_2(\text{OH})_2^{4+}$, which we shall call the "dimer," is diamagnetic. The forward reaction (3) has been shown to be endothermic, with $\Delta H \approx 9.8$ kcal. per mole. Thus, the dimer is more stable at higher temperatures, in the room temperature range.

(1) Important references are given by Hedström.³

(2) G. A. Gamlen and D. O. Jordan, *J. Chem. Soc.*, 1435 (1953).

(3) B. O. A. Hedström, *Ark. fur Kemi*, **6**, 1 (1953).

We have also studied the absorption spectra in the ultraviolet, of the above solutions at 15 and 51°, and in some cases at 25°. The spectra show peaks at $240 \pm 0.5 \text{ m}\mu$ and $335 \pm 0.5 \text{ m}\mu$. We have established that the peak at $335 \text{ m}\mu$ is almost entirely due to the dimer, and that the one at $240 \text{ m}\mu$ is due to contributions both from Fe^{3+} and FeOH^{2+} . The results have been used to evaluate $K_{2,2}$ at 15 and 51°, and these are found to be in agreement with those obtained from the magnetic data. The value obtained at 25° from magnetic data is in reasonable agreement with that reported by Hedström.

This work adds to the small group of known substances or ions in which exchange effects destroy all the paramagnetism normally present in iron (III). It also suggests that the well known subnormal magnetic moment for the iron in hydrous ferric oxide⁴ may be due to part of the iron being present as dimers built into the gel structure. Just prior to precipitation almost half the iron in a 0.04 *M* solution is present as dimer.

This work was performed under contract with the Signal Corps Engineering Laboratories, Army Signal Corps.

(4) P. W. Selwood, M. Ellis and K. Wethington. *THIS JOURNAL*, **71**, 2181 (1949).

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FUROCHROMONES AND COUMARINS. XI.
THE MOLLUSCIDICAL ACTIVITY OF BERGAPTEN,
ISOPIMPINILLIN AND XANTHOTOXIN

Sir:

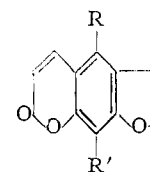
Though several thousands of synthetic organic compounds have been screened for molluscicidal activity, very little is known about the activity of naturally occurring compounds. We have investigated the molluscicidal activity of the naturally occurring furocoumarins, *e.g.*, bergapten (I), isopimpinillin (II) and xanthotoxin (III) against *Biomphalaria boissi*, the intermediate host of *Schistosoma mansoni* (Bilharzia) in Egypt. It was found that the molluscicidal power of bergapten and isopimpinillin is of the same order of magnitude as that of the most powerful synthetic organic compounds, *e.g.*, dinitro-*o*-cyclohexylphenol and sodium pentachlorophenate, I being stronger than II, III being less potent. I, II and III are neither caustic nor irritating as is the case with many synthetic molluscicides.

These findings may explain—at least in part—the role of furocoumarins in the vegetable kingdom (protection of plants against snails) and may open a new method in the control of *Biomphalaria boissi*, namely, by growing plants which contain these active furocoumarins and after harvesting throwing the plants into the channels infected by the snails (*Biomphalaria boissi*).

Egyptian plants are known to contain active furocoumarins, *e.g.*, *Ammi majus* L contains xanthotoxin.¹

(1) A. Schönberg and A. Sina. *Nature*, **161**, 481 (1948).

I, R = OCH₃, R' = H
II, R = R' = OCH₃
III, R' = OCH₃, R = H



The results of our preliminary experiments were confirmed and extended by Dr. G. T. Evans and Mr. R. Zachary from the United States Naval Medical Research Unit No. 3 (Cairo) to whom we are greatly indebted. Their results are given below:

Test Conditions.—Compare D. O. Hoffman and R. Zachary, *Am. J. Trop. Med. and Hyg.*, **2**, 332 (1953). Test temperature 26°. Exposure period 24 hours in the presence of the chemical followed by 72 hours observation period in fresh pond water.

Chemical solutions were made in acetone, an aliquot taken and diluted to the desired concentration. The solvent in itself was not toxic to snails at the dose used.

Snails used were obtained from a drain (natural habitat) near the village of Geziret Mohammed and stocked in out-door concrete ponds fitted for snail colonization. Natural water was used after being filtered through a cotton layer. The percentage figures refer to snails killed.

TABLE I

Compound	p.p.m. = parts per million	
	5 p.p.m.	2 p.p.m.
I	32/32 (100%)	22/32 (69%)
II	22/32 (69%)	3/32 (9%)
DCHP ²	13/16 (81%)	14/32 (44%)
DOW G ³	10/16 (63%)	2/32 (6%)

III in a concentration of 10 p.p.m. and under the above conditions killed only 25% (4/16) of the snails tested and 0% (0/16) in a concentration of 5 p.p.m. The kill was 100% (10/10) when the concentration was 50 p.p.m. and the exposure and observation periods were 24 hours.

(2) DCHP = Dinitro-*o*-cyclohexylphenol, R. E. Kuntz, *The Lebanese Medical Journal*, **46** (1952); R. E. Kuntz and M. A. Stirewalt, *Proc. Helminth. Soc. Washington*, **17**, 95 (1950).

(3) Dow G. = Sodium pentachlorophenate, A. Halawani, N. Latif and T. Anwar, *J. Roy. Egypt. Med. Assoc.*, **34**, 163 (1951); E. G. Berry, M. O. Nolan and O. Gonzales, *Health Repts.*, **65**, 939 (1950).

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THE ACTION OF OXALYL CHLORIDE ON
INDOLES: A NEW APPROACH TO TRYPTAMINES

Sir:

Interest in the physiological actions of tryptamine derivatives has been stimulated considerably by the proposals of Woolley and Shaw¹ and Gaddum² that serotonin (I) may play a role in central nervous system function. The possibility that the remarkable hallucinogenic effects of lysergic acid diethylamide may be due to its effect as a serotonin antimetabolite has been proposed.^{1,2} These

(1) D. W. Woolley and E. Shaw, *Brit. Med. J.*, **122**–126 (1954).

(2) J. H. Gaddum, *Ciba Foundation Symposium*, London (1953).