mation of ferric hexafluoroacetylacetonate. In the absence of ultraviolet light no reaction was evident even after 40 hr. at 80°. Moreover, continuous irradiation of the solution was found necessary since cessation of the reaction occurred when the irradiation was interrupted. At higher temperatures, on the other hand, such as in refluxing toluene or the dimethyl ether of diethylene glycol, the thermal reaction becomes more important, as would be expected, and the effect of ultraviolet light less pronounced.

In contrast to the clean reactions of iron and chromium carbonyls, the carbonyls of molybdenum and tungsten gave labile products with 1,3-diketones. Molybdenum carbonyl and acetylacetone produced the air-sensitive Mo(III) acetylacetonate,[4] while only an oxyacetylacetonate was isolated from the reaction of tungsten hexacarbonyl and acetylacetone.[15]

It was found that the reactivity of the active hydrogen compound paralleled its acidity; with the following order of decreasing reactivity prevailing for the photochemical reaction of iron pentacarbonyl in benzene.

	hfaH >	$(C_6H_5CO)_2CH_2$ >	AAH >	8-hydroxyquinoline
$t_{1/2}$, hr.	2	6	7	13
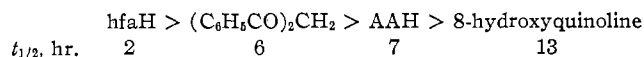
The reactivity of the metal carbonyls with acetylacetone in benzene or isopropyl ether under ultraviolet irradiation decreased qualitatively as follows.

$$Fe(CO)_5 > W(CO)_6 > Mo(CO)_6 \gg Cr(CO)_6$$
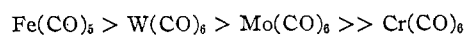
The effect of different solvents on the photochemical reaction of iron pentacarbonyl with acetylacetone in the refluxing solvent was

	CCl_4 >	C_6H_6 >	isopropyl ether >	THF
$t_{1/2}$, hr.	3	7	8	48
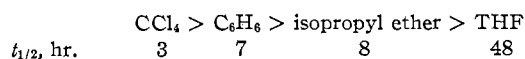
The results obtained in carbon tetrachloride require some comment. Although chromic acetylacetonate was obtained in good yield from this solvent, the reactions of the other metal carbonyls employed in this study were complicated by side reaction with the carbon tetrachloride to produce hydrogen chloride and the metal chlorides.

Efforts to produce mixed carbonyl acetylacetonates, such as $Fe(CO)_2(AA)_2$, by photochemical reaction of the metal carbonyl with the required amount of the 1,3-diketone have thus far given only the simple chelate. However, studies with bistriphenylphosphine iron tricarbonyl have shown that the triphenylphosphine ligand is considerably less labile than the CO ligand to displacement by diketones. Photochemical reaction of bistriphenylphosphine iron tricarbonyl with two moles of hexafluoroacetylacetone in 1:1 benzene–methylene chloride solution resulted in a yellow solid, m.p. 183–185° (from the filtrate), which possessed triphenylphosphine but no CO ligand.[17] Contact of bistriphenylphosphine iron tricarbonyl with acetylacetone, on the other hand, under similar conditions resulted in little or no reaction.

(17) Elemental and infrared analyses suggest the product to be primarily $(C_6H_5)_3PFeCl_2$.

In conclusion, it appears from this and other work currently in progress in our laboratory that this reaction should be of broad synthetic value.

Magnetic and Electric Properties of Monosulfides and Mononitrides of Thorium and Uranium

BY R. DIDCHENKO AND F. P. GORTSEMA

In connection with studies of the electric and magnetic properties of rare earth monosulfides and nitrides,[1] it was established using the Gouy method that EuS, contrary to the earlier measurements of Klemm,[2] is ferromagnetic with a Curie point at 18°K., in excellent agreement with the recent findings of McGuire, *et al.*[3] Extension of the studies of the monosulfides and nitrides of uranium and thorium, which, like their rare earth counterparts, crystallize in a NaCl lattice, revealed that US is also ferromagnetic with a Curie point at 180°K. and a molar susceptibility of 6280×10^{-6} e.m.u. at 298°K. ($\mu^B = 2.46$), in disagreement with previous values,[4,5] while ThS and ThN are diamagnetic. The metallic components of these materials are thus present in the +4 state.

The magnetic behavior in the U–N system is more complicated, as may be seen from Fig. 1. Samples of the indicated composition were obtained by thermal decomposition of UN_2, which, in contrast to previous claims,[6] can be prepared easily by passing ammonia gas over UH_3 while raising the temperature to 1000°. This has been confirmed by analysis and X-ray data, which showed the presence of a face-centered cubic lattice with $a_0 = 5.300 \pm 0.005$ Å., in excellent agreement with the value of Rundle[6] for UN_2 prepared by a high pressure method. The magnetic susceptibility measurements on this phase were rather irreproducible but showed definitely that the Curie–Weiss law was not obeyed. Phases of the compositions $UN_{1.83}$ and $UN_{1.22}$ were obtained reproducibly by heating UN_2 in a tantalum crucible in argon for 4 hr. to 1250 and 1900°, respec-

(1) R. Didchenko and F. P. Gortsema, *J. Phys. Chem. Solids*, to be published.

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(3) T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, *Appl. Phys. Letters*, **1**, 17 (1962).

(4) E. D. Eastman, L. Brewer, L. A. Bromley, P. W. Gilles, and N. L. Lofgren, *J. Am. Chem. Soc.*, **72**, 4019 (1950).

(5) M. Picon and J. Flahaut, *Bull. soc. chim. France*, 772 (1958).

(6) R. E. Rundle, *et al.*, "The Uranium Nitrogen System, Chemistry of Uranium," Collected Papers, Report TID 5290, U. S. Atomic Energy Commission, 1958, p. 53.
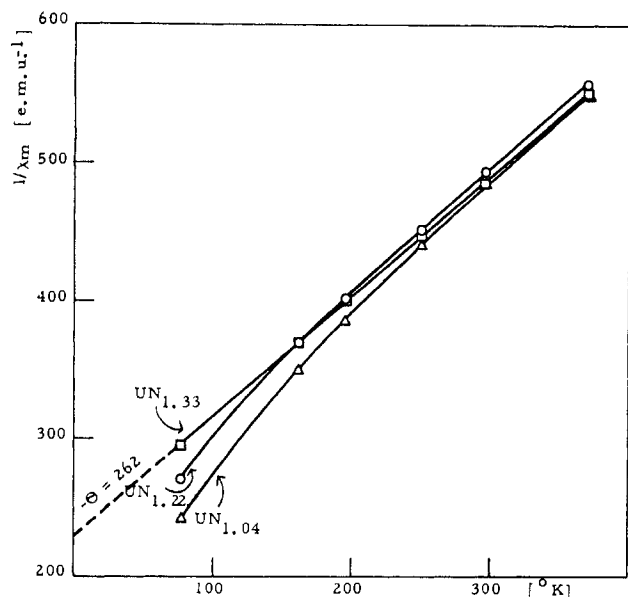
Fig. 1.—Plot of $1/\chi_m$ vs. T for uranium nitride samples of different composition.

tively; $UN_{1.04}$ results after 3 hr. *in vacuo* at 1950°. Above that temperature the material disappears rapidly. All these phases had a face-centered cubic lattice with $a_0 = 4.875 \pm 0.005$ Å.; their magnetic behavior was, however, markedly different. While $UN_{1.33}$ (U_3N_4) is clearly antiferromagnetic with a Weiss constant $\theta = -262$, the phases with lower nitrogen content behave in a manner characteristic of ferrimagnetic materials.[7] These values have been obtained reproducibly on several samples of the same composition, prepared in different ways. The Bohr magneton number $\mu_B = 3.04$ for U_3N_4, when compared with the

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literature values of 2.4 for $U(C_2O_4)_2$, 2.92 for UCl_4, 3.22 for UCl_3, and 3.12 for UO_2, does not allow an unambiguous assignment of an oxidation state to the uranium atoms. Neither is this possible on the basis of ionic radii, although if one assigns to the nitrogen a radius of 1.40 Å., which is characteristic of conductive rare earth nitrides, the resulting radius of 1.04 Å. for uranium agrees very well with Goldschmidt's value for U^{+4}.

Furthermore, the ferrimagnetic behavior of lower nitrides may be best explained by the presence of a sublattice of U^{+3} which would tend to form and grow as the nitrogen content is decreased. This assumption of mixed valency states is not inconsistent with the electrical properties of these compounds, which may be treated in a manner analogous to rare earth nitrides and sulfides.[1,8]

The monosulfide and the mononitride of thorium are electronic conductors with a low specific resistivity ($\sim 10^{-4}$ ohm-cm.) and a Seebeck coefficient of a few μvolts per degree at room temperature. The uranium compounds have been studied in more detail on sintered powders. Using previously described apparatus,[1] we have found that between room temperature and 1300°K. the resistivity increases very slightly: from 0.9 to 1.4×10^{-4} ohm-cm. for UN and from 3.6 to 4.3 $\times 10^{-4}$ ohm-cm. for US. Both materials are p-type conductors with a room temperature thermoelectric power of about $+50$ μv./deg., which reaches a peak value of 80 μv./deg. for US and 100 μv./deg. for UN around 700°K. and then decreases back to the room temperature value at 1300°K. No change in the temperature coefficient of resistivity has been found for US at the Curie point.

(8) J. W. McClure, *J. Phys. Chem. Solids*, to be published.

Correspondence

Infrared Spectra of Ethylenediamine-tetraacetic Acid (EDTA)

Sir:

A controversy still exists concerning the structure of EDTA (H_4Y).[1-5] We wish to report data which not only support structure I, recently proposed for solid H_4Y, but also allow a better understanding of the problems involved in the interpretation of infrared spectra of EDTA compounds.

In this laboratory we have prepared five different solid hydrochlorides of H_4Y, three of which are listed in Table I.

From Bellamy's correlations for carboxylic acids and α-amino acids,[6] it follows that the single band near

(1) D. Chapman, *J. Chem. Soc.*, 1766 (1955).
(2) D. H. Busch and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **75**, 4574 (1953).
(3) R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, 1, 174 (1962).
(4) K. Nakamoto, Y. Morimoto, and A. E. Martell, *J. Am. Chem. Soc.*, **85**, 309 (1963).
(5) D. T. Sawyer and J. E. Tackett, *ibid.*, **85**, 314 (1963).
(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

TABLE I

COMPOSITIONS OF SOLID PROTONATED EDTA COMPOUNDS

		C	H	Cl	N
$H_4Y \cdot 2HCl$	Calcd.	32.89	4.97	19.42	7.67
	Found	33.1	4.9	19.5	7.8
$H_4Y \cdot 2HCl \cdot 2H_2O$	Calcd.	29.94	5.53	17.67	6.98
	Found	29.8	5.9	17.3	6.7
$H_4Y \cdot HCl \cdot H_2O$	Calcd.	34.64	5.52	10.23	8.08
	Found	34.6	5.5	10.2	7.8
		34.7	5.6	10.5	8.2

TABLE II

CARBONYL FREQUENCIES OF SOLID PROTONATED EDTA COMPOUNDS[a]

Compound	Frequency, cm.$^{-1}$
H_4Y	1689 s
$H_4Y \cdot 2HCl$	1736 s
$H_4Y \cdot 2HCl \cdot 2H_2O$	1724 sh
	1712 sh
	1695 s
$H_4Y \cdot HCl \cdot H_2O$	1724 s

[a] s, sharp; sh, shoulder.