the reactions of an optically active complex with ligands of known configuration and those of doubtful configuration. On the other hand, in the communication by Bailar and Gott, the complex $[Co(l\text{-pn})_2CO_3]^+$ containing two molecules of *l*-propylenediamine was found to coördinate preferentially with the *d*-forms of tartaric, lactic and α-chloropropionic acid. In the present investigation a copper complex containing *d*-tartaric acid seems to favor the formation of complexes with *d*-pn. It may be, however, that the configurations of complexes of different metals with the same optically active ligand may differ, or may form complexes with either configuration.[8] The configuration of the same compound may vary at different[9] temperature or *p*H, so it seems necessary to run the same reactions under widely different experimental conditions. The reaction mechanism in these cases, when studied, will probably throw more light on the matter.

We wish to thank the National Science Foundation and the University of Illinois for grants to one of us (Das Sarma).

URBANA, ILLINOIS

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[8] F. M. Jaeger and H. B. Blumendal, *Z. anorg. allgem. Chem.*, **175**, 161 (1928); J. Lifschitz, *Z. physik. Chem.*, **114**, 485 (1925).

[9] Sister Mary Martinette and J. C. Bailar, Jr., THIS JOURNAL, **74**, 1054 (1952).

[CONTRIBUTION FROM THE KNOLLS ATOMIC POWER LABORATORY,[1] GENERAL ELECTRIC COMPANY]

The Uranyl Cupferrates

BY WILLIAM S. HORTON

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It is shown that the complex formed between uranyl ion and cupferron (ammonium nitrosophenylhydroxylamine) crystallizes in the cubic system with $a_0 = 13.3$ Å. and space group T^4-$P2_13$. Because of the space group symmetry the UO_2 group is linear and the three cupferron residues must be equivalent. Therefore the compound may be called ammonium uranyl cupferrate, $NH_4[UO_2(C_6H_5N_2O_2)_3]$. The symmetry of the space group also requires that the arrangement of the oxygen atoms with respect to the central uranium atom be a trigonal bipyramid in case the coördination number is five, and either a cube or dodecahedron for coördination number eight. The information presently available cannot distinguish these. The uranyl cupferrate group is sufficiently stable to form compounds also with sodium, potassium, rubidium and cesium in the place of the ammonium ion. On the other hand, the hydrogen compound decomposes slowly on standing. A lithium compound has not been successfully separated. Methods for preparing these compounds are given. The aqueous solubilities appear to be moderately small.

Introduction

Since Baudisch[2] introduced cupferron (ammonium nitrosophenylhydroxylamine), it has been used for a variety of analytical separations. Uranium is an interesting example since in strongly acid solution U(VI) (as UO_2^{++}) does not precipitate but U(IV) does. The fact that uranyl ion does form a complex with cupferron was discovered quite early[3] but went more or less unnoticed until recently when it was found to be the source of minute traces of uranium extracted from an acid solution by an organic solution of cupferron.[4] It is also interesting that, like 8-quinolinol, cupferron provides three groups to the complex although the uranyl ion is divalent.

The direct preparation of this complex was found to be relatively simple and to lead to crystals of the cubic system. In view of the stability of the compound to 200°, which greatly contrasts with other cupferrates, a crystallographic and chemical investigation was undertaken to learn more of its nature. As will be seen, this led to the discovery of a group of compounds which may be called "uranyl cupferrates" somewhat analogous to the uranyl acetates and uranyl nitrates.

Crystallography of Ammonium Uranyl Cupferrate.[5]—By mixing a methanol (or ethanol) solution of uranyl nitrate hexahydrate with a solution of cupferron in 50% aqueous methanol, an orange yellow precipitate is obtained in good yield. The dried crystals occasionally appear as tiny cubes when viewed under the microscope. They are isotropic to polarized light, and have a refractive index of about 1.53. Hull–Debye–Scherrer X-ray diffraction patterns, taken with filtered copper radiation in a 114.59 mm. camera, gave the d-spacings listed in Table I, where they may be compared with those calculated for a cell edge of 13.28 Å. These spacings verify the cubic nature of the unit cell, and since only the 100 reflection was absent the cell is primitive. An experimental specific gravity, determined by flotation to be 2.02, agrees with that calculated for four molecules per cell—1.98.

Easily prepared (although of poor shape) single crystals were obtained by slow evaporation of a saturated methanol solution. One was mounted in a Weissenberg camera and eventually oriented to rotate about a 100 axis. The zero-level Weissenberg photograph, when indexed, showed systematic absences for *h*00 reflections with *h* odd. Therefore the crystallographic space group is either T^4-$P2_13$ or O^2-$P4_23$. These space groups may be distinguished by locating the four uranium atoms in the unit cell since these are necessarily at the fourfold positions: $x, x, x;\ ^1/_2 - x, \bar{x}, ^1/_2 + x;\ \bar{x}, ^1/_2 + x, ^1/_2 - x;\ ^1/_2 + x, ^1/_2 - x, \bar{x}$ for $T^4 - P2_13$ and $^1/_4, ^1/_4, ^1/_4;\ ^1/_4, ^3/_4, ^3/_4;\ ^3/_4, ^3/_4, ^1/_4;\ ^3/_4{:}\ ^1/_4, ^3/_4$ for $O^2 - P4_23$. A Patterson *hkO* projection was calculated using zero-level Weissenberg intensities determined visually with the multiple-film technique. The results are shown in Fig. 1, where the units shown on the contours are arbitrary. The peak at

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[1] The Knolls Atomic Power Laboratory is operated by the General Electric Company for the Atomic Energy Commission. The work reported here was carried out under Contract No. W-31-109 Eng-52.

[2] E. Bamberger and O. Baudisch, *Chem. Z.*, **33**, 1298 (1909).

[3] O. Baudisch and R. Furst, *Ber.*, **50**, 324 (1917).

[4] (a) N. H. Furman and D. R. Norton, MDDC 1623, April, 1947; (b) N. H. Furman, W. B. Mason and J. S. Poklea, *Anal. Chem.*, **21**, 1325 (1949).

[5] The assistance of C. W. Tucker, Jr., and P. Senio, Fuels Research Unit of this Laboratory with this phase of the investigation is gratefully acknowledged.

TABLE I

d-SPACINGS OF AMMONIUM URANYL CUPFERRATE

d, Å. Obsd.	Calcd.	*hkl* Assignment	Intensity
9.36	9.39	110	V.S.
7.62	7.67	111	S$^+$
6.59	6.64	200	M
5.88	5.94	210	V.S.$^+$
5.39	5.42	211	S$^-$
4.72	4.70	220	V.W.$^-$
4.43	4.43	221, (300)[a]	S$^+$
4.19	4.20	310	S
3.98	4.00	311	W
3.82	3.83	222	M
3.67	3.68	320	M$^-$
3.54	3.55	321	V.S.$^-$
3.32	3.32	400	W
3.22	3.22	410, 322	M
3.13	3.13	411, 330	W$^+$
3.05	3.05	331	M
2.89	2.90	421	M$^+$
2.87	2.83	332	V.W.
2.72	2.71	422	M$^+$
2.66	2.66	430, (500)[a]	W
2.61	2.60	510, 431	S
2.56	2.56	511, 333	M
2.47	2.47	520, 432	W$^+$
2.43	2.42	521	W
2.35	2.35	440	V.W.$^-$
2.31	2.31	522, 441	V.W.$^-$
2.28	2.29	530, 433	V.W.$^-$
2.22	2.21	600, 442	M$^-$
2.16	2.15	611	S$^-$
2.08	2.07	540, 443, 621	S
2.07	2.05	541	V.W.
1.984	1.980	542, 630	W
1.964	1.958	631	W
1.927	1.917	444	V.W.

[a] Weissenberg photographs showed that *h*00 reflections with *h* odd are absent.

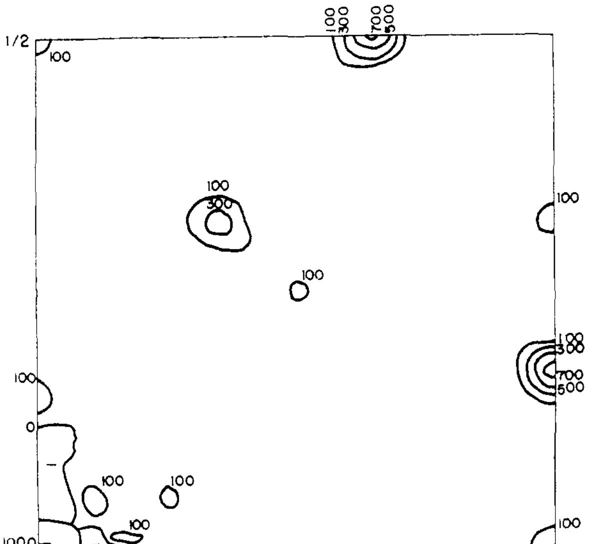

Fig. 1.—Patterson *hk*0 projection.

the origin is merely indicated. The three major peaks are found at about 1/3, 1/2; 1/2, 1/6; and 1/6, 1/3. Because of the large atomic scattering factor for uranium as compared with the scattering factors for the other atoms in the crystal, these peaks undoubtedly correspond to uranium-uranium interatomic vectors. This determines T^4 as the correct space group with the parameter $x = 0.162$[6] locating the uranium atoms. The other space group, O^2, would give strong peaks at 0, 1/2; 1/2, 1/2; and 1/2, 0, two of which are found to be rather weak and the other is missing altogether. Further this space group would not account for the observed strong peaks.

With the space group unambiguously determined the symmetry of the molecule may be partially assigned. The molecule centered about the uranium at *x*,*x*,*x*, situated on the threefold axis, the cube body diagonal, will serve as the prototype of all. The two uranyl oxygen atoms must also lie on this axis in order to maintain the threefold symmetry. This agrees with the conclusion, already established by Fankuchen[7] and Zachariasen,[8] that the uranyl group is generally linear. The ammonium nitrogen must also be on this axis for the same reason, no doubt with the hydrogens arranged tetrahedrally—one of these on the axis too. To maintain the threefold symmetry the cupferron residues, $C_6H_5N_2O_2$, must be arranged symmetrically about the axis and must be equivalent. For this reason, and for reasons of chemical reactivity to be discussed below, the cupferron complex of UO_2^{++} must be considered different in type from the oxine complex containing three reagent residues. In that case thermal decomposition data indicates that one oxine may be treated as a molecule of crystallization. In the case of cupferron the combination must be considered as $UO_2(C_6H_5N_2O_2)_3$, an anionic group.

Preparation of the Uranyl Cupferrates.—The method used to prepare ammonium uranyl cupferrate, the compound considered above, no doubt can be used for the hydrogen and alkali metal analogs. In general the procedure is to make the corresponding hydrogen or alkali metal cupferrate and to use this in place of cupferron. One way to make the alkali cupferrates is to use the corresponding hydroxide to replace ammonia from cupferron. Salting out the product by common ion effect apparently gives a quicker but less productive procedure than boiling off the ammonia. The hydrogen cupferrate (phenylnitrosohydroxylamine) may be prepared by the action of dilute acetic acid on an aqueous cupferron solution. However, it must be used within a few hours because of its instability. This method was used to prepare the ammonium, sodium and potassium salts.

Another method involves metathesis between sodium uranyl cupferrate and a soluble salt of the alkali metal. By this method rubidium and cesium uranyl cupferrates have been produced. The sodium salt is the most soluble and therefore the best to use here. Aqueous or alcohol-water solutions may be used.

A third method, displacement of ammonia from ammonium uranyl cupferrate by alkali hydroxide, has been tried without success. While ammonia was evolved for a time, the other products were not identifiable. In general, the yields by the first two methods were good: the ammonium compound, 86%; sodium, 89 to 100%; potassium, 64%; rubidium, 83%; and cesium, 91%. A 10% excess of one reagent was usually used.

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[6] There is a fourfold ambiguity with respect to this parameter but no ambiguity in distinguishing T^4 from O^2.

[7] I. Fankuchen, *Z. Krist.*, **9**, 473 (1935).

[8] W. H. Zachariasen, *Acta Cryst.*, **1**, 277 (1948).

Ammonium and sodium uranyl cupferrates were analyzed in detail to verify the correctness of the formulas. Others were analyzed merely for alkali metal (or for uranium in the case of the hydrogen compound) since the method of preparation and this determination are sufficient to identify the compound once the first two compounds are established. For the ammonium compound the results were: U, 33.7% (34.0 calcd.); C, 30.4 (30.9); H, 2.8 (2.7); N, 14.2 (14.0); for the sodium compound: U, 34.1 (33.8); C, 30.7 (30.7); H, 2.2 (2.2); N, 12.3 (11.9); Na, 3.5 (3.3); potassium compound: K, 5.1 (5.4); rubidium compound: Rb, 10.6 (11.2); cesium compound: Cs, 15.8 (16.3). Alkali metals were determined with a flame photometer, carbon and hydrogen by the usual microcombustion technique, nitrogen by a micro-Dumas method, and uranium by reduction to U(IV) and titration to U(VI).[9]

Hydrogen uranyl cupferrate, prepared from nitrosophenylhydroxylamine and uranyl nitrate, gave an initial uranium analysis of 36.2% (34.9 calcd.) but on standing this rose to 52.0% after about five weeks indicating marked decomposition at room temperature.

Attempts to prepare lithium uranyl cupferrate, both from lithium cupferrate and by metathesis with sodium uranyl cupferrate, were not completely successful. The first method gave one substance containing about 0.7% lithium (1.01 calcd.) and another containing no detectable lithium. Metathesis gave the material containing 0.7% lithium. Various attempts at purification failed to produce a higher lithium content in this material. Probably a more complex compound is involved.

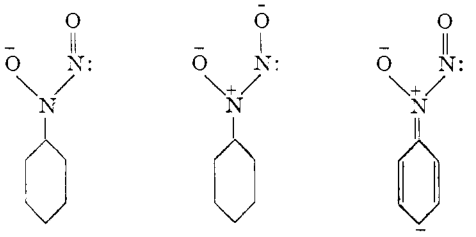
Properties of the Uranyl Cupferrates.—A characteristic of all the uranyl cupferrates considered here, except the hydrogen compound, is their stability. Generally, the cupferrates of the heavy elements are not used as weighing forms in chemical analysis because they lack this property. On the other hand, ammonium uranyl cupferrate can be heated to almost 200° before the decomposition sets in, leading to U_3O_8.

A cursory examination of the powder diffraction patterns of the sodium, potassium rubidium and cesium uranyl cupferrates indicated that only the last two are of the cubic system.

The crystalline solids have colors ranging from yellow to red-orange. Dilute aqueous solutions are yellow, alcohol solutions are red-orange. Approximate aqueous solubilities are, respectively, 2, 7, 0.7, 0.4 and 0.2 mmoles per liter for the ammonium, sodium, potassium, rubidium and cesium uranyl cupferrates at room temperature.

Discussion

The structure of the uranyl cupferrate group presents interesting problems. The crystallographic symmetry and the preparative chemical reactions lead one to attempt treating it as an entity. Presumably it is similar to the uranyl acetate group of sodium uranyl acetate[6] or to the trinitrato-uranyl group of rubidium uranyl nitrate.[10] In the former case the acetate ion was assumed to be symmetrical and was found by packing considerations to form a bridge between adjacent uranium atoms and uranyl oxygens on different uranium atoms. The three nitrate groups of rubidium uranyl nitrate are coplanar with the uranium atom and the combination more nearly represents a distinct group than in the case of the acetate. In both of these examples the non-uranyl oxygens are equivalent by virtue of resonance. The cupferrate oxygens are not equivalent although they may become somewhat similar in the external bonding characteristics because of resonance among the structures shown below.



There are no facts known at this time which distinguish whether the oxygen atoms are arranged similar to either sodium uranyl acetate or rubidium uranyl nitrate. An alternate structure may be correct with the nitrosyl oxygen not strongly bound. In the former case the total coördination number of the uranium atom would be eight, in the latter case five. Because of the required symmetry of the group, the only feasible arrangements for eight are the cube and dodecahedron and for five the trigonal bipyramid. For the cube, f-orbitals must participate, but for the others they may or may not.[11,12] The symmetry of the group is C_3 for a coördination of eight and either C_3 or C_{3h} for a coördination of five. Weissenberg data have been taken and are being processed to deduce as much of the crystal structure as possible in an attempt to locate these oxygen atoms.

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[9] The assistance of the Analytical Chemistry groups of the General Electric Research Laboratory and this Laboratory are gratefully acknowledged.

[10] J. L. Hoard and J. D. Stroupe, Atomic Energy Project Report A-1229, Dec. 1, 1943; or see "Spectroscopic Properties of Uranium Compounds," G. H. Dieke and A. B. F. Duncan, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 15-35.

[11] G. E. Kimball, *J. Chem. Phys.*, **8**, 188 (1940).

[12] M. G. Shirmazan and M. E. Dyatkina, *Zhur. Fiz. Khim.*, **27**, 481 (1953).