

Table I. Nonphotochemical Hydrogen Abstraction Using Diethyl Azodicarboxylate

Starting material	Procedure	Time, hr	Product	Yield, %
Ethanol	A	72	Acetaldehyde ^a	62
Isopropyl alcohol	A	48	Acetone ^a	84
Cyclohexanol	A	72	Cyclohexanone ^a	55
Benzyl alcohol	B	5	Benzaldehyde ^a	60
<i>p</i> -Nitrobenzyl alcohol	B	5	<i>p</i> -Nitrobenzaldehyde	57
α -Methylbenzyl alcohol	B	10	Acetophenone	87
Benzhydrol	B	10	Benzophenone	70
Hydrazobenzene	B	0.5	Azobenzene	98
Anisidine	B	5	4,4'-Azodianisole	28
Ethanethiol	A	48	Ethyl disulfide	90
2-Propanethiol	A	72	Isopropyl disulfide	70
2-Propene-1-thiol	A	0.5	Allyl disulfide	90
1-Dodecanethiol	B	5	Dodecyl disulfide	95
<i>t</i> -Dodecyl mercaptan	B	10	<i>t</i> -Dodecyl disulfide	70
Benzenethiol	A	24	Phenyl disulfide	90
<i>p</i> -Nitrobenzenethiol	D ^b	8	<i>p</i> -Nitrophenyl disulfide	Not measured
<i>o</i> -Aminobenzenethiol	B	4	<i>o</i> -Aminophenyl disulfide	67
2-Naphthalenethiol	C	5	2-Naphthyl disulfide	87
2-Mercaptobenzothiazole	B	0.5	2,2'-Dithiobisbenzothiazole	95

^a Isolated as the semicarbazone. ^b Ethanol was used as solvent.

+0.408, respectively, in units of β , and from this fact it would be predicted that they might have a high tendency to abstract hydrogen atoms from hydrogen donors.

Schenck and Formanek³ first reported the photochemical dehydrogenation with diethyl azodicarboxylate (**1**); they found that photochemical reaction of **1** with isopropyl alcohol gave pinacol and tetraethyl tetraazetetracarboxylate, and acetaldehyde and **1** gave diacetyl and diethyl hydrazodicarboxylate (**2**). Recently, and concurrently with the present work, Cookson, *et al.*,⁴ reported the photochemical oxidation of ethanol and cyclohexanol with **1** to give acetaldehyde and cyclohexanone. We have extended the usefulness of this reagent in a dehydrogenation reaction which may serve as a basis for preparative procedures. It has now been found that **1** is a useful oxidizing agent involving hydrogen abstraction from hydrogen donors, with good agreement with the quantum chemical prediction stated above. In this communication we wish to describe a new nonphotochemical hydrogen-abstracting oxidation using diethyl azodicarboxylate (**1**).

Compound **1** reacts smoothly with a wide variety of primary or secondary alcohols, mercaptans, anilines, and hydrazobenzenes to form aldehydes or ketones, disulfides, azobenzenes, and azobenzenes, respectively, while it itself undergoes hydrogenation to diethyl hydrazodicarboxylate (**2**). The reaction can be performed either by keeping the thoroughly mixed starting materials with 1 equiv of **1** in the dark at room temperature for 1 to 3 days (procedure A), or by refluxing the starting material with 1 equiv of **1** in anhydrous benzene for 0.5 to 10 hr (procedure B). Chloroform can be employed as the solvent (procedure C), and potentially other solvents may be used. The completion of the reaction is characterized by a change in color from orange red to pale yellow. Representative (not optimum) examples are listed in Table I.

(3) G. O. Schenck and H. Formanek, *Angew. Chem.*, 70, 505 (1958).

(4) R. C. Cookson, I. D. R. Stevens, and C. T. Watt, *Chem. Commun.*, 259 (1965). They also found that the reaction of cyclohexanol and **1** to give cyclohexanone and **2** proceeds in the dark, although in poor yield.

The reaction of hydrazobenzene with **1** proceeds remarkably rapidly even in cold benzene to give azobenzene and **2** in almost quantitative yield. This would be connected with the strong electron-donating property of hydrazobenzene, and in fact the latter has an occupied antibonding orbital (-0.495β) according to Hückel MO method.

We consider this hydrogen-abstracting reaction as possessing considerable potential synthetic utility because of the mildness of the conditions employed and the good yields obtained. Moreover, it is noteworthy that **1** has no oxygen atoms which are available for oxidation; accordingly, this reaction does not proceed further after abstraction of hydrogen.

An investigation of the mechanism of these reactions and the reaction of other azo-disubstituted derivatives such as azodicarbonitrile, azodiacyl, and 4-phenyl- Δ^1 -1,2,4-triazoline-3,5-dione² with electron donors is in progress.

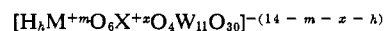
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A New General Structural Category of Heteropolyelectrolytes. Unusual Magnetic and Thermal Contraction Phenomena¹

Sir:

This is to report an extensive investigation which establishes a new general structural category of heteropolyelectrolytes. The formula of the anions is



Some of the salts have unusual physical properties.

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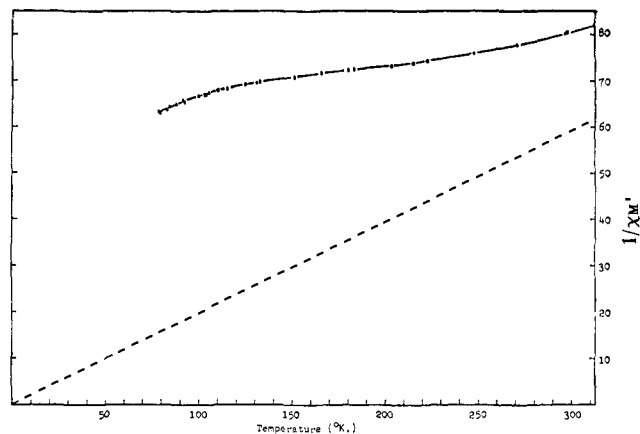


Figure 1. Experimental Curie plot for potassium salt of anion 5 (solid line). Expected Curie plot if interactions were absent (broken line). χ_M' is the molar susceptibility (in cgs units), corrected for diamagnetism and for temperature-independent paramagnetism of tetrahedral Co(III) and octahedral Co(II).

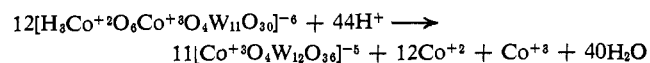
The anions' structure is a modification of the well-known "Keggin" structure.²⁻⁶ An octahedrally coordinated metal ion, M^{+m} , replaces just one of the 12 octahedral W atoms of the conventional Keggin structure. The X occupies the Keggin unit's central tetrahedral cavity. In some cases X consists merely of two H atoms, fulfilling the same role as the two H atoms are presumed to do within metatungstate ion, $[H_2W_{12}O_{40}]^{-6}$, which has the Keggin structure.³ The number of other H atoms, H_h (which must be firmly attached to exterior oxygen atoms of the complex, most probably to those surrounding M), seems to be mainly characteristic of the identity of M^{+m} .

Fifteen salts have been analyzed for complexes wherein

- anion 1: M = Co⁺², X = Si⁺⁴ (ref 7)
- anion 2: M = Co⁺³, X = H₂⁺² (ref 8)
- anion 3: M = Ga⁺³, X = H₂⁺² (ref 9)
- anion 4: M = Co⁺², X = Co⁺² (ref 7, 10)
- anion 5: M = Co⁺², X = Co⁺³ (ref 7, 10)

We are pursuing good qualitative evidence for other combinations. Anions 4 and 5 above were originally erroneously formulated as 12-tungstodibaltates by the present first author.^{10,11}

- (2) J. F. Keggin, *Proc. Roy. Soc. (London)*, **A144**, 75 (1934).
- (3) R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934).
- (4) L. C. W. Baker and V. E. Simmons, *J. Am. Chem. Soc.*, **81**, 4744 (1959).
- (5) N. F. Yannoni, Doctoral Dissertation, Boston University, 1961.
- (6) L. C. W. Baker in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 608.
- (7) V. E. Simmons, Doctoral Dissertation, Boston University, 1963.
- (8) M. Shibata and L. C. W. Baker, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960.
- (9) O. W. Rollins, Doctoral Dissertation, Georgetown University, 1965.
- (10) L. C. W. Baker and T. P. McCutcheon, *J. Am. Chem. Soc.*, **78**, 4503 (1956).
- (11) The analytical discrepancy is small (11:1 = 12:1.09). The dicobalt complexes each react rapidly with acid to yield, quantitatively, undoubted^{4,5} 12-tungsto Keggin structures, e.g.



Because the cubic unit cell of each dicobalt derivative is F-centered and all of the odd-order reflections are extremely weak, the powder

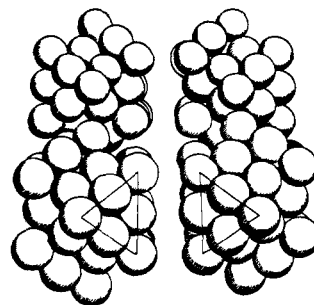


Figure 2. Keggin-like units in half of the F-centered cubic unit cell, showing their alternating orientations. The four complexes shown are in the same horizontal plane. The balls represent the anions' oxygen atoms. The small W and M atoms are in octahedral interstices between the oxygen atoms. The viewer is looking diagonally down, directly into the channel between the two rear complexes. The lower half of a large octahedral pocket, bounded by reentrant faces, is seen between the four complexes. Two flat faces of the two nearest Keggin-like units are identified by triangles. These are two of the eight flat faces which bound one of the other sort of large octahedral pockets, which lie between unit cells of the type illustrated.

The complexes are best formed in nearly neutral solutions. All react rapidly with H⁺ except anion 2 (*cf.* the inertness of Co(III)O₆ bonds). Salts of anions 2 and 3 are diamagnetic. Anions 4 and 5 exhibit very strong intraionic paramagnetic interactions.⁷ The paramagnetic susceptibility of the latter changes⁷ only 13% between -143 and 23°, a phenomenon for which we know no parallel (see Figure 1). The spectra⁷ confirm the electronic interactions, coordination geometries, and oxidation states (also shown by oxidation-reduction analysis) for the cobalt complexes. The degree of aggregation is exactly confirmed by cryoscopy in fused Na₂SO₄·10H₂O^{9,12} and by potentiometric titrations. Density measurements combine with X-ray data to check the 11-tungsto formulas within 0.5%.

The K⁺, NH₄⁺, Rb⁺, and Cs⁺ salts of anions 2, 3, 4, and 5 form isomorphous cubic crystals containing the Keggin-like units in an array not described for any salts of conventional 12-heteropoly Keggin units.

Single crystal X-ray work shows that isomorphous F-centered cubic crystals, containing alkali cations and eight anions per unit cell, exist for anions 2, 3, 4, and 5 at temperatures below 20°. For each salt the space group is one of the following: F43m, Fm3m, Fm3, F432, or F23. Examinations with a polarizing microscope show that the crystals are isotropic.

For the ammonium salt of anion 5, electron density maps directly reveal the positions of the W atoms, the tetrahedral Co atom, and the 40 oxygen atoms in the anion. Refinement in Fm3m gave $R = 14.7\%$ for all (232) reflections measured. New data have been collected and a more rigorous refinement is in process.

For each complex in the crystals, an M^{+m} ion randomly occupies one of the 12 positions which would be filled by W atoms in a conventional Keggin unit. The other 11 positions are filled by W atoms. Adjacent Keggin-like units differ in orientation by a 90°

X-ray pattern (originally used) is virtually identical with that of a primitive cell with an edge half as long. Crystallographic symmetry based on the erroneous primitive cell, consequently derived from the powder X-ray work, therefore indicated 12 W atoms.

- (12) G. A. Tsigdinos, Doctoral Dissertation, Boston University, 1961.

rotation about one of the axes which correspond to the fourfold inversion axes of a conventional Keggin unit. This produces the F-centering (see Figure 2). Therefore, the arrangement resembles an enlarged NaCl structure, with the Na⁺ ions replaced by a set of Keggin-like units having one orientation and the Cl⁻ ions replaced by Keggin-like units with an orientation at right angles to the first set. This arrangement makes possible some extraordinary thermal properties.

Adjacent Keggin-like structures in such an arrangement each have six oxygen atoms (in two parallel rows of three each) which project closest to the corresponding six oxygen atoms from the next Keggin-like structure, thus forming a channel between the four parallel rows (three oxygen atoms in each row). These channels are of appropriate size for water molecules, H-bonded together, and H-bonded *very* weakly⁶ to the oxygen atoms of the complexes.

A Keggin structure has two sets of tetrahedrally oriented faces. One set consists of four "flat faces" of the complex. Each flat face consists of six close-packed oxygen atoms in a planar triangle. The other set of tetrahedrally oriented faces consists of four "re-entrant faces," that is, faces with deep indentations in their centers.

In the structure described (see Figure 2), two types of rather large octahedral pockets (big enough for the cations and hydrate H₂O's) are formed between the complexes. One type is bounded by the flat faces of the eight adjacent Keggin-like units. The other type of large pocket is similarly bounded by eight reentrant faces. The channels between the anions interconnect the large pockets.

The electron density maps, for crystals X-ray photographed at 25–32°, show that the channels and large pockets contain electron density, but it is smeared out on the maps, with the exact locations of cations and H₂O's not evident. This is probably the characteristic result of disorder in those spaces.

Unusual Thermal Behavior. When the cubic salts are heated or desiccated, the crystals shrink reversibly. At about 45°, each has changed so that it no longer has an F space group, although it is still cubic. A cubic cell containing eight complexes has a definitely shorter edge than at low temperature (*e.g.*, 15°) and high humidity.

The case of (NH₄)₇Na₂[GaO₆H₂O₄W₁₁O₃₀]·15H₂O is especially interesting. An air-dried sample of this solid has a unit cell edge which shrinks rapidly, reversibly, and *continuously*, *e.g.*, from 22.17 Å at 10° to 21.84 Å at 47° (a 4.6% shrinkage in volume). The cell edge immediately returns reproducibly to a given value for each temperature. The cell is cubic at all times. Most of the change occurs between 25 and 40° (see Figure 3). The change was monitored by taking, at various temperatures, single crystal X-ray photographs and complete powder patterns, and by observing the effect on a single sharp powder line for which 2θ moved from 63.3 to 64.4°. The line never decreased in intensity or broadened, but shifted continuously through several times its width as the temperature varied.¹³

A probable explanation would depend upon reversible

(13) A powder pattern of NaCl in the same apparatus did not change with temperature.

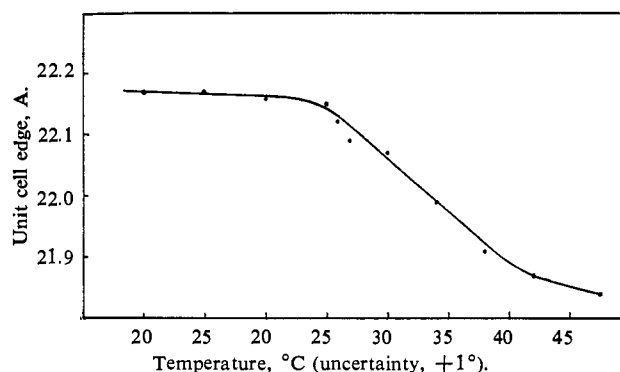


Figure 3. Continuous and reversible shrinkage of the cubic unit cell edge with increasing temperature for an air-dried sample of (NH₄)₇Na₂[GaO₆H₂O₄W₁₁O₃₀]·15H₂O. Thermal equilibrium had been attained at each point.

thermal disorganization of H-bonding patterns of H₂O molecules (and NH₄⁺ ions) in the large octahedral pockets and/or the channels, allowing the heteropoly complexes to move continuously closer as the temperature goes up. This bears a rough analogy to the much less dramatic shrinkage of liquid water upon heating from 0 to 4°. Reversible movement of H₂O molecules from the channels into vacancies in the large octahedral pockets (in the case of a partly dried crystal) might also be involved. A more exhaustive investigation is underway.

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Pentadienyl Cations and Their Rearrangements in FSO₃H–SbF₅ Solution¹

Sir:

The solvent system FSO₃H–SbF₅ is one of the most acidic media yet studied. It has been shown to be an extremely useful solvent for studying carbonium ions.^{2a,b} Using this method^{2b} we have now studied the pentadienyl cations I and IV and their rearrangements. Ions I and IV are readily and clearly formed by dissolving the precursor dienols in FSO₃H–SbF₅ at –75 to –60°. Previous work has shown that in 96% H₂SO₄ at –30° only III is observed.³ In FSO₃H at –50° although ion I is observed initially it readily rearranges to II and then very quickly to III.⁴ In FSO₃H–SbF₅, I is stable for hours at –75°, but at 10° R₁ has *t*_{1/2} = 185 sec. Ion II is stable at –10° and III is only formed by prolonged warming at 35°, R₂ *t*_{1/2} = 8 to 12 min. In contrast to FSO₃H alone, these rates

(1) Stable Carbonium Ions. XXVI. Part XXV: G. A. Olah and M. S. Comisarow, *J. Am. Chem. Soc.*, in press.

(2) (a) T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **42**, 502 (1964); (b) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).

(3) T. S. Sorensen, *Can. J. Chem.*, **42**, 2768 2781 (1964).

(4) T. S. Sorensen, *ibid.*, **43**, 2744 (1965).