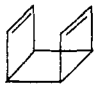
and characterized by glpc, ir, and nmr. Glpc analysis (mol/100 mol **2**) exhibited the following: acetylene (1.2), vinylacetylene (2.6), butadiene (3.8), benzene (5.3), cyclooctatetraene (0.2), and styrene (0.9). These determinations were confirmed by a less precise nmr analysis. No *anti* or *syn* dimer of cyclobutadiene (**3**) could be detected either by glpc or nmr. Finally, a copious iron-containing deposit formed in the oven during the pyrolysis.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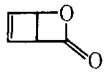
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The results of our previous work on the FVP of photo-α-pyrone (**4**)[1] can be summarized for comparison. A *m/e* 52 fragment was thermally generated having a low ionization potential (8.2 eV) and diradical character on the basis of its dimerization and reactivity with radicals and oxygen. Chemical experiments showed that rapid quenching of the pyrolysate gave the *syn* dimer of cyclobutadiene (**3**) exclusively while benzene and acetylene were formed either in the gas phase or on warm walls prior to quenching. No vinylacetylene, butadiene, or other C_4 fragment was detected. On the basis of these experiments, we concluded that the transient *m/e* 52 thermal product was cyclobutadiene, and that this has a significant but short lifetime at FVP conditions.

In contrast, we believe that the appearance potential measurements, radical titration experiments, and chemical experiments all indicate that the only C_4H_4 product which survives the pyrolysis of **2** is vinylacetylene. The absence of the *syn*-dimer **3** in the rapidly quenched pyrolysate is particularly significant.

The different behavior of **2** and photo-α-pyrone (**4**) under FVP conditions most likely involves both surface thermal activation and decomposition for the former and only surface thermal activation for the latter. This would allow for the highly exothermic formation of metallic iron from **2** and is consistent with the copious deposition of iron on the oven surface as well as the low yield of organic products.[9] The precise nature of the reactions leading to vinylacetylene, benzene, acetylene, cyclooctatetraene, and styrene is extremely interesting, but obscure. Any surface reaction must occur very rapidly owing to the short residence times of activated molecules on the hot oven walls.

We must conclude that Li and McGee[4a,b] also did not detect cyclobutadiene from the low-pressure pyrolysis of **2** in contrast to their claim. Their ionization potential measurement for the *m/e* 52 fragment (9.6 eV) from **2** is much closer to vinylacetylene (9.9 eV) than cyclobutadiene (8.2 eV).[1] Furthermore their fragmentation pattern for *m/e* 52, which was obtained after subtraction of the fragments due to 1,3-butadiene, was essentially the same as that for vinylacetylene except for the low masses: for *m/e* 52 from **2**, *m/e* (relative intensity) 52 (100), 51 (59), 50 (51), 49 (17), 48 (1), 39 (5), and 26 (26); for vinylacetylene, 52 (100), 51 (56), 50 (49), 49 (19), 48 (8), 39 (1), and 26 (12). Finally, their reported ionization potential for C_8H_8 (9.1 eV) is very different from that of **3** (8.4 eV) as well as cyclooctatetraene and styrene (8.86 eV).[7]

Acknowledgment. We wish to thank Professor Leo Paquette for supplying us with our initial sample of cyclobutadieneiron tricarbonyl.

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[9] Nickelocene was also found to undergo surface decomposition at FVP conditions.[5,10]

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E. Hedaya, I. S. Krull,[11] R. D. Miller[12]
M. E. Kent, P. F. D'Angelo, Paul Schissel
Union Carbide Research Institute
Tarrytown, New York 10591

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Molecular Structure of the Decamolybdodicobaltate(III) Ion

Sir:

When solutions of cobalt(II) ion and heptamolybdate ion ($Mo_7O_{24}{}^{6-}$) are mixed in the presence of an oxidizing agent (such as bromine), Kurnakov,[1] Hall,[2] and others found that an emerald green complex is formed as the main product, namely, the heteropoly complex ion hexamolybdocobaltate(III), which forms salts such as $(NH_4)_3[H_6CoMo_6O_{24}]\cdot 12H_2O$. Friedheim and Keller[3] showed that at the same time a small amount of another complex is also formed, having a Co:Mo ratio of 1:5. Tsigdinos, *et al.*,[4] found that if a hot solution of the hexamolybdocobaltate complex ion is treated with activated charcoal or Raney nickel the 1:6 complex is converted almost entirely to the 1:5 complex. These workers[4] proved the latter to be a dimer, and formulated the ammonium salt (earlier prepared by Friedheim and Keller[3]) as $(NH_4)_6[Co_2Mo_{10}O_{36}]\cdot 10H_2O$. We have now completed a crystal structure analysis of this interesting compound, which shows the proper formula to be $(NH_4)_6[H_4Co_2Mo_{10}O_{38}]\cdot 7H_2O$.

Solutions of the complex ion deposit large black crystals of two different ammonium salts, as follows: form A, monoclinic, space group C2/c or Cc, $a = 44.18 \pm 0.03$ Å, $b = 12.60 \pm 0.01$ Å, $c = 15.36 \pm 0.01$ Å, $\beta = 106.89 \pm 0.02°$, $Z = 8$, $V = 4 \times 2044$ Å^3; form B, monoclinic, space group Pc, $a = 12.59 \pm 0.01$ Å, $b = 12.72 \pm 0.01$ Å, $c = 15.48 \pm 0.01$ Å, $\beta = 121.70 \pm 0.01°$, $Z = 2$, $V = 2110$ Å^3.

The two forms may appear simultaneously, though form A seems to be the more stable, especially in warm solutions. Our study was carried out on form B (prepared from a sample kindly supplied by Drs. Tsigdinos and Baker), to which the formula given applies. Using Mo Kα radiation, 4105 X-ray intensity data were collected for this crystal with a Picker automatic diffractometer. The data were normalized and subjected to the symbolic addition procedure of phase determination, assuming the space group to be P2/c. A structure was readily found in this way, but complete convergence of the refinement to $R = 0.071$ could only be accomplished in space group Pc. In the refinement, individual, isotropic thermal parameters were assumed, and no corrections were made for absorption, extinction, or dis-

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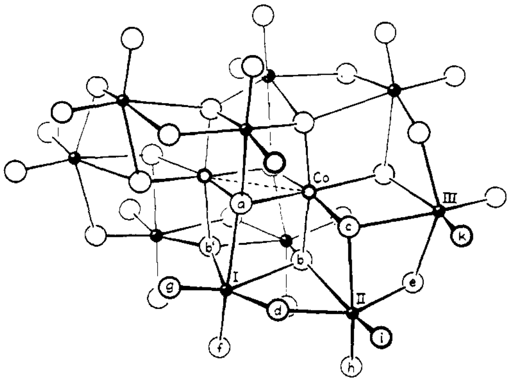

Figure 1. Pictorial view of the decamolybdodicobaltate(III) ion, $[H_4Co_2Mo_{10}O_{38}]^{6-}$.

persion. It was found that the axis of the molecule that is vertical in Figure 1 is tilted away from the pseudo-twofold crystal axis by about 2.5°.

The heteropoly molecule ion, $[H_4Co_2Mo_{10}O_{38}]^{6-}$, conforms closely to an ideal point symmetry 222 (D_2). Thus, the crystal is a raceme, and it may be possible to resolve the complex into optically active components. The structure of the molecule (see Figure 1) may be considered as being derived from the flat, trigonal hexamolybdocobaltate(III) ion (analogous to hexamolybdotellurate ion[5] by removing one MoO_2 group from each of two hexa molecules, turning one 180° around a CoO_6 octahedron diagonal, and joining them so that the two CoO_6 octahedra come together at the center, sharing an edge.

Table I gives the interatomic distances in the decamolybdodicobaltate(III) molecule, averaged over four determinations each, according to the ideal symmetry. The range of individual measurements (standard error of each ± 0.03 Å) is shown, and these are about what would be expected to result from ionic and hydrogen bond interactions with the irregular crystal structure environment. There seems no reason to suppose that D_2 symmetry is not assumed by the free ion in solution. Of particular interest is the Co–Co environment at the center of the molecule. The Co–Co distance (dashed line in Figure 1) is 2.779 ± 0.007 Å and the Co–O_a bond length is 1.889 ± 0.015 Å. These lengths may be compared with those in the dinuclear μ-dihydroxy-bis(tetraammine)dicobalt(III) ion as found by Prout[6] in his crystal structure determination of $[(NH_3)_4Co(OH)_2Co(NH_3)_4]Cl_4 \cdot 4H_2O$, in which the Co–Co length is 2.932 ± 0.005 Å and the Co–OH length is 1.912 ± 0.010 Å.

Table I. Bond Lengths in the Decamolybdodicobaltate(III) Molecule Ion, Averaged over D_2 Symmetry[a]

Bonded atoms	Max var in crystal, Å	Av bond length, Å
Co—O_a	0.025	1.89
O_b	0.045	1.90
O_c	0.051	1.95
Mo_I—O_a	0.082	2.31
O_b	0.060	2.26
O'_b	0.035	2.01
O_d	0.039	1.89
O_f	0.074	1.67
O_g	0.021	1.71
Mo_{II}—O_b	0.065	2.30
O_c	0.055	2.26
O_d	0.019	1.95
O_e	0.017	1.91
O_h	0.051	1.73
O_i	0.066	1.71
Mo_{III}—O_c	0.114	2.28
O_e	0.101	1.97
O_k	0.051	1.71

[a] See Figure 1.

An outstanding feature of the crystals of both form A and form B is an extreme pleochroism. The optic directions are nearly parallel to the molecular twofold axes, and are blue (vertical in the figure), red (horizontal, normal to the Co–Co axis), and olive yellow (parallel to the Co–Co axis).

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Howard T. Evans, Jr.
U. S. Geological Survey, Washington, D. C.

John S. Showell
National Science Foundation, Washington, D. C.

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Degradation of Polyphosphates in Solution. IV. Catalytic Effects of Divalent Metal Ions on Trimetaphosphate Formation

Sir:

It has been shown that the aqueous acid-catalyzed degradation of linear long-chain polyphosphates proceeds *via* four major routes: (1) hydrolytic scission in the interior of the chain to produce two shorter chains; (2) hydrolytic scission of the chain at an end group with the production of orthophosphate; (3) splitting off of trimetaphosphate from an end of the chain; and (4) splitting out of trimetaphosphate from the interior of the chain.[1,2] There have been a number of reports that the formation of the degradation products is significantly accelerated by polyvalent metal ions,[3-7] but very little is known about the pathways of these catalytic processes. Such information is especially desirable for the reactions leading to trimetaphosphate formation because of their biological implications. While trimetaphosphate itself is not known to form in living systems, its production from linear polyphosphates involves the biologically significant formation of a P–O–P linkage, a reaction which in nature appears to need the presence of a divalent metal ion.[8]

We have carried out exploratory studies on the effect of several divalent metal ions on the rate of formation of trimetaphosphate, and our findings may be summarized as follows. (1) The catalytic effects are highly specific and apply only to reactions occurring at the ends of the chains, where rate increases of up to more

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