spectrum of the filtrate was identical to that of 1,10-undecadiene.

Determination of Unsaturation in the Soluble Poly-α-diolefins. Quantitative Infrared Spectrometry.—Quantitative measurements of the intensity of the absorption due to unsaturation in the soluble polymers were made at 967 cm.$^{-1}$, corresponding to the *trans* form of olefins of the type RCH=CHR', and at 910 cm.$^{-1}$, corresponding to the vinyl group, $RCH{=}CH_2$.

The measurements were carried out using an automatic-recording Perkin-Elmer single-beam infrared spectrometer, model 12B, modified for double-pass operation and equipped with sodium chloride optics. The methods used were similar to those described by Treumann and Wall.[26] All measurements were carried out in carbon disulfide solution, using a sodium chloride cell of 1.002 mm. inside thickness and a slit width of 0.400 mm.

The system was calibrated at 967 cm.$^{-1}$, using *trans*-4-methylpentene-2[27] as a standard. Measurements of the optical densities of solutions of this compound in carbon disulfide over a concentration range of 0.005 to 0.04 M gave a value for the molar absorptivity, ϵ, of 137 liters/mole-cm. Hampton[28] states a value of 139 for the absorptivity of *trans*-olefins at 967 cm.$^{-1}$.

The calibration of the system at 910 cm.$^{-1}$ was accomplished in the same manner, using 1-octadecene,[29] 1,8-nonadiene, 1,13-tetradecadiene and 1,21-docosadiene as standards. The absorbancy *versus* molarity (of olefin) curves based on these results are superimposable and linear at molarities below 0.04. The molar absorptivity was calculated to be 152 liters/mole-cm. Hampton[28] reports a value of 155 for the absorptivity of terminal olefins at 910 cm.$^{-1}$.

The measurements of *trans* and terminal unsaturation in the soluble polymers was carried out as follows. A solution of the polymer, 0.02–0.07 molar in monomer units, was made up in carbon disulfide. The absorbancy of the solution was measured both at 967 and at 910 cm.$^{-1}$. The molar concentrations of *trans* and of terminal olefin were calculated by dividing the absorbancies measured at 967 and at 910 cm.$^{-1}$ by 13.7 and 15.5, respectively. The average amount of each type of double bond per monomer unit was calculated by dividing the molarity of the polymer solution (expressed in monomer units) into the molar concentration of the appropriate double bond. The results of these determinations are listed in Table XIII.

Quantitative Bromination.—The measurement of total unsaturation in the soluble polymers using iodine monobromide (Hanus solution) was carried out according to the method described by Siggia.[22] The results of these determinations are listed in Table XIII.

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(26) W. B. Treumann and F. T. Wall, *Anal. Chem.*, **21**, 1161 (1949).

(27) The authors are grateful to Dr. John E. Mahan of the Phillips Petroleum Co. for a sample of 99.53% pure *trans*-4-methylpentene-2.

(28) R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

(29) The authors are grateful to John Rogers for a sample of pure 1-octadecene.

URBANA, ILL.

COMMUNICATIONS TO THE EDITOR

HETEROPOLY TUNGSTOCOBALTATE ANIONS CONTAINING RESPECTIVELY Co(II) AND Co(III) IN CoO_4 TETRAHEDRA. I. 12-TUNGSTOCOBALTOATE AND 12-TUNGSTOCOBALTIATE[1]

Sir:

In a previous paper,[2] a system of four chemically interrelated heteropoly tungstocobaltate anions was reported. The isomorphous structures of $[Co^{+2}Co^{+2}W_{12}O_{42}]^{-8}$ and $[Co^{+2}Co^{+3}W_{12}O_{42}]^{-7}$ were considered in detail. The other two anions[3] are $[Co^{+2}O_4W_{12}O_{36}]^{-6}$ and its isomorph, $[Co^{+3}O_4W_{12}O_{36}]^{-5}$. This paper reports several proofs of the formulas and structure of the two monocobalt anions.

The significant feature of the results lies in the fact that the cobalt atoms are shown conclusively to be located within CoO_4 tetrahedra. So far as we have been able to ascertain, these are: (a) the first complex ions known to contain Co(III) in *any* tetrahedral site and (b) the first complex ions known to contain Co(II) within a tetrahedron of oxygen atoms which is unequivocally perfectly regular.[4]

Because of the electronic configuration of cobalt, these soluble complexes have various interesting implications for ligand field theory. Also, evaluation of the strength of the ligand field produced by oxygen atoms which are simultaneously attached to other atoms (W) of high oxidation state is possible. This facilitates better understanding of heteropoly electrolytes and perhaps of certain oxides.

Both anions have perfect tetrahedral symmetry; therefore no distortion of the central CoO_4 tetrahedra should occur in solution, except insofar as introduced by the electronic structure of the cobalt. Anionic distortion can also be caused by packing forces in some crystals.

We have proven the structure of the anion by several lines of evidence[6]:

(a) A geometrical argument establishes, for $[X^{+v}W_{12}O_{40}]^{-(8-v)}$, that the central atom lies within a tetrahedron of oxygens, provided all tungstens are within octahedra each of which shares at least one oxygen with the central polyhedron.[7] The structure is identical to that deduced by Keggin and others[8] for $[PO_4W_{12}O_{36}]^{-3}$ and similar anions (see point "e"). Formula proof rests upon: (A) analyses, including establishment of oxidation states; (B) potentiometric titrations which establish that each anion contains just 40 oxygen atoms provided neither contains constitutional water; and (C)

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(1) This research was supported in part by the U. S. Atomic Energy Commission, through Contract AT(30-1)-1853.

(2) L. C. W. Baker and T. P. McCutcheon, THIS JOURNAL, **78**, 4503 (1956).

(3) In the earlier paper[2] the obsolete Miolati–Rosenheim formulation was deliberately used for the monocobalt anions because the correct formulas were unknown.

(4) No Jahn–Teller effect is expected for Co(II) in a tetrahedral field, because the ground state is not orbitally degenerate.[5]

(5) C. J. Ballhausen and C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

(6) Detailed discussion of each of these results and its implications will be included in papers soon to be published.

(7) This condition is assumed because it obtains in every heteropoly tungstate (and molybdate) structure investigated to date.

(8) J. F. Keggin, *Nature*, **131**, 908 (1933); *Proc. Roy. Soc.* (*London*), **A144**, 75 (1934); J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935); J. L. Hoard, *Z. Krist.*, **84**, 217 (1933); J. deA. Santos, *Revista Faculdade Cienc., Univ. of Coimbra* (*Portugal*), **16**, 5 (1947); R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934); L. C. W. Baker, "Properties of Heteropoly Molybdates," Climax Molybdenum Company Information Bulletin Cdb-12 (1956).

careful dehydration experiments which show that salts can be dehydrated completely without decomposing the anions. Techniques were similar to those utilized for other compounds.[9,10,11] (b and c) The tetrahedral central grouping is unequivocally supported by the paramagnetic susceptibilities and absorption spectra.[6] (d) Unlike many octahedral cobaltic complexes,[12] the 12-tungstocobaltiate is reduced reversibly and practically instantaneously to the cobaltous complex. Various potentiometric titrations establish the formal oxidation potential in N H_2SO_4 as -1.0 volt. Extrapolated potentials of mixtures in pure water yield the same result. Thus the coördination provides relatively small stabilization for the $+3$ oxidation state. These observations are consequences of the tetrahedral coördination or, conversely, they support that configuration.[6] (e) Using single crystal X-ray techniques, a detailed structure for potassium 12-tungstocobaltiate has been determined in this laboratory by Klaas Eriks, Nicholas F. Yannoni, and ourselves. Every atom in the anion is unambiguously located. The anions are discrete and slightly squeezed in one direction in that salt.

These results[13] show that the simplest relationship exists between the condition of these heteropoly electrolytes in solution and in the solid state. This point has caused concern to many investigators of heteropoly electrolytes.

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(9) L. C. W. Baker and T. P. McCutcheon, *Anal. Chem.*, **27**, 1625 (1955).

(10) L. C. W. Baker, B. Loev and T. P. McCutcheon, THIS JOURNAL, **72**, 2374 (1950); L. C. W. Baker, G. A. Gallagher and T. P. McCutcheon, *ibid.*, **75**, 2493 (1953).

(11) L. C. W. Baker, *et al.*, *ibid.*, **77**, 2136 (1955).

(12) L. E. Orgel, *Inst. intern. Chim. Solvay*, **10^e** *Conseil Chim. Brussels*, 289 (1956).

(13) Detailed measurements of the magnetic susceptibilities, spectra, and x-ray crystal structure are well advanced for the two dicobalt anions mentioned in the first paragraph. These will be the subjects of other papers.

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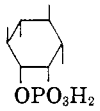
SYNTHESIS OF AN OPTICALLY ACTIVE *myo*-INOSITOL 1-PHOSPHATE

Sir:

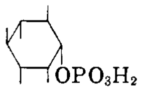
In a recent paper[1] the characterization of *myo*-inositol 1-phosphate resulting from the base hydrolysis of soybean phosphoinositide was reported. This natural substance showed $[\alpha]_D$ $+3.4°$ (*p*H 9, water) and $[\alpha]_D$ $-9.8°$ (*p*H 2, water), and, partly because of this optical activity, we concluded that the diacyl glycerol phosphate moiety in the original phosphoinositide must have been linked to the 1-position of the *myo*-inositol ring.

It can be argued that the optical activity observed was so small that it may have been due to an impurity. To check this point, we have carried out the synthesis of an *asymmetric* *myo*-inositol 1-phosphate. The starting material was galactinol,[2] which has been shown to be 1-*O*-α-D-galactopyranosyl *myo*-inositol.[3] Complete benzylation of this compound, and then methanolysis of the galactosidic linkage, gave 2,3,4,5,6-penta-*O*-benzyl *myo*-inositol. Phosphorylation of this product with diphenyl phosphorochloridate and hydrogenolytic removal of the benzyl and phenyl groups gave a *myo*-inositol 1-phosphate which was isolated as a crystalline cyclohexylamine salt. *Anal.* Calcd. for $C_{18}H_{39}O_9N_2P$: N, 6.1; P, 6.8. Found: N, 5.7; P, 6.6. The substance showed $[\alpha]_D$ $-3.2°$ (*p*H 9, water) and $[\alpha]_D$ $+9.3°$ (*p*H 2, water). Its infrared spectrum (KBr pellet) and chromatographic properties were identical with those of the substance isolated from soybean phosphoinositide. Thus, this synthetic compound is the enantiomorph of the soybean compound. and the good check between the rotations of the two establishes the optical purity of the latter. This result, coupled with the recent work of Brockerhoff and Hanahan,[4] leaves little doubt that the *myo*-inositol portion of soybean phosphoinositide is substituted in one of its enantiomeric 1-positions.

The absolute configuration of the 1-position of *myo*-inositol to which the galactosyl unit is attached in galactinol is known, and was shown[3] to be that one which by inversion leads to (−)-inositol. Thus, the absolute configurations in the two enantiomeric *myo*-inositol 1-phosphates also are now established, and are represented by the formulas



Synthetic compound



Soybean compound

Although there is no generally accepted convention by which one can assign configurational names to these isomers, the proposal of Lardy[5] would lead to designating the synthetic compound as D-*myo*-inositol 1-phosphate and the one from soybean phosphoinositide as L-*myo*-inositol 1-phosphate.

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(1) F. L. Pizer and C. E. Ballou, THIS JOURNAL, **81**, 915 (1959).

(2) R. J. Brown and R. F. Serro, *ibid.*, **75**, 1040 (1953).

(3) E. A. Kabat, D. L. MacDonald, C. E. Ballou and H. O. L. Fischer, *ibid.*, **75**, 4507 (1953).

(4) H. Brockerhoff and D. J. Hanahan, *ibid.*, **81**, 2591 (1959).

(5) H. A. Lardy, in "The Vitamins," Vol. 11, edited by W. H. Sebrell, Jr., and R. S. Harris, Academic Press, Inc., New York, N. Y., 1954, p. 325.

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VINCA ALKALOIDS.[1] IV. STRUCTURAL FEATURES OF LEUROSINE AND VINCALEUKOBLASTINE, REPRESENTATIVES OF A NEW TYPE OF INDOLE-INDOLINE ALKALOIDS

Sir:

In the preceding communication[1] we were able to demonstrate that the new alkaloids, leurosine and vincaleukoblastine, probably are isomeric $C_{46}H_{58}O_9N_4$ compounds. The spectral properties of the two compounds indicated striking similarities in their structures. We wish to present evidence that these two compounds are representatives of a new class of dimeric alkaloids containing both indole and dihydroindole moieties.

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(1) Vinca Alkaloids. III. N. Neuss, M. Gorman, G. H. Svoboda, G. Maciak and C. T. Beer, THIS JOURNAL, **81**, 4754 (1959).