Table I

Temp, °C	Product	$^{14}C/^{3}H$	Yield,[a] % *Via* anhydride	 *Via* DCC
5	**3**	1.18	66	59
	4	1.19	20.5	18
	5	0.84	13	21
			Total 99.5	98
30	**3**	1.14	57	51
	4	1.34	23	17
	5	0.90	15	19
			Total 95	87

[a] By isotope dilution and scintillation counting.

agent of the DCC reaction. A maximum of 55% (5°) to 60% (30°) can be calculated as the extent of the anhydride's participation during peptide synthesis in solution with DCC. Delayed addition of the amine component,[2] or solid phase peptide synthesis, during which the amine component is anchored to an insoluble support is expected to decrease the importance of path a and increase the extent of anhydride participation. Experiments on the solid phase are in progress.

$$\underset{(1\ \text{equiv})}{^{14}\text{C(Z-Gly)}_2\text{O}^{11}} + \underset{(1\ \text{equiv})}{\text{DCC}} + \underset{(30\ \text{equiv})}{^{3}\text{HZ-Gly-OH}} +$$

$$\underset{(10\ \text{equiv})}{\text{Gly-OEt}} + \underset{(10\ \text{equiv})}{\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2} + \underset{(10\ \text{equiv})}{\text{C}_6\text{H}_5\text{NH}_2}$$

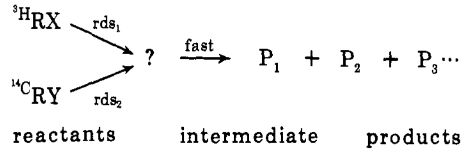
$$\Big\downarrow \begin{smallmatrix}\text{CH}_2\text{Cl}_2\\ 10\ \text{hr}\end{smallmatrix}$$

$$\underset{\mathbf{3}}{\text{Z-Gly-Gly-OEt}} + \underset{\mathbf{4}}{\text{Z-Gly-NHC}_6\text{H}_5} + \underset{\mathbf{5}}{\text{Z-Gly-NHCH}_2\text{C}_6\text{H}_5}$$

(both labels)

While this technique borrows heavily from classical product distribution analyses, several unique advantages arise through the use of distinctly labeled reactants for the study of systems which can be generalized as in Scheme II. (1) The reactions for which a common intermediate is suspected may be run simultaneously, *in the same solution*, thus maintaining identical conditions for both reactions. (2) The scope of manageable product distributions is considerably expanded through the determination of products by isotope dilution. (3) The relative rates, rds_1/rds_2, of formation for any product can be assessed directly from the $^{3}H/^{14}C$ activity ratio of that product. The tremendous range of available tritium activities, *ca.* 10^8, can be exploited to ensure that these ratios are readily measurable even if the slower reaction attains only a few per cent completion. (4) The $^{3}H/^{14}C$ ratios of the products reveal the presence (or absence) of a common intermediate.

Scheme II



Although the present study used an isolable intermediate (the anhydride) directly, the method is of potential utility for the study of such reactive species as carbenes, carbenoids,[12] and "dark" *vs.* photochemical intermediates.[13]

Acknowledgment. Generous financial support of this work by the Eli Lilly Co. is gratefully acknowledged.

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(11) Prepared as described in ref 5.

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(13) H. E. Zimmerman and G. A. Epling, *ibid.*, **94**, 7806 (1972).

(14) National Science Foundation Undergraduate Research Participant, Summer 1972.

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A Tetranuclear Copper(I) Complex. The Crystal and Molecular Structure of the 2:1 Derivative of Copper(I) Iodide and Bis(diphenylphosphino)methane

Sir:

Copper(I) halides react with bis(diphenylphosphino)methane (DPM) and 1,2-bis(diphenylphosphino)ethane (DPE) giving compounds with several stoichiometries, $(CuX)_nL_m$ (L = DPM, DPE and X = Cl, Br, I). The preparation and characterization of these complexes have recently been reported.[1] The crystal and molecular structure of $(CuCl)_2DPE_3$ have also been determined,[2] revealing binuclear centrosymmetric molecules with tetrahedral copper atoms bridged by one DPE molecule, the other two of which act as chelate ligands. However, many obscurities still remain in the structure and behavior of this series of complexes. Therefore we have undertaken a systematic study of the structure of such compounds by single-crystal X-ray analysis. We report here the preliminary structural results on $(CuI)_2DPM$.

The prismatic crystals, elongated along [100], were found to be orthorhombic, with cell parameters $a = 17.128 \pm 0.009$, $b = 18.306 \pm 0.009$, and $c = 16.508 \pm 0.008$ Å. Space group *Pbca* was indicated by systematic absences. The density 1.94 ± 0.01 g/cm^3, as determined by flotation, is in agreement with the calculated value of 1.960 g/cm^3 with eight formula units of $(CuI)_2DPM$ in the cell.

Intensity data ($\theta \leqslant 30$) were collected on a Siemens automated diffractometer with Mo Kα-filtered radiation using the θ–2θ scan technique. Independent reflections (1336) with $I > 3\sigma_I$ were corrected for Lorentz and polarization factors. Although the adsorption coefficient is 43 cm^{-1}, no correction was applied because of the small size of the crystal (nearly a cylinder of 0.15 mm of diameter), the adsorption correction factor A^* ranging from 1.65 to 1.64 in the θ range of interest. The structure was determined by the heavy-atom method and refined to a present value of the conventional R index of 0.065, by the full-matrix least-squares method with anisotropic temperature factors for the iodine and copper atoms.

The crystals consist of discrete centrosymmetric dimetric units of $[(CuI)_2DPM]_2$ arranged around the crystallographic symmetry center to form a parallelogram

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(1) N. Marsich, A. Camus, and E. Cebulec, *J. Inorg. Nucl. Chem.*, **34**, 933 (1972).

(2) V. Albano, P. L. Bellon, and G. Ciani, *J. Chem. Soc., Dalton Trans.*, 1938 (1972).

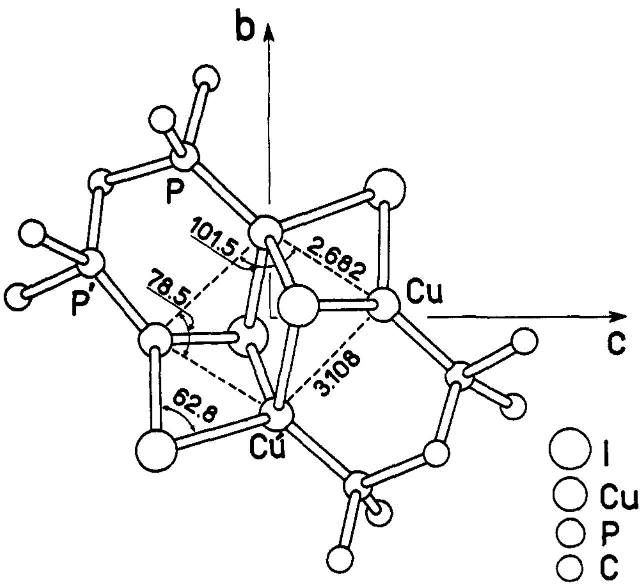

Figure 1. The molecule viewed along the cystallographic *a* axis. Only the first carbon atom of each phenyl group is shown.

of copper atoms, with Cu–Cu distances of 2.682 (7) and 3.108 (7) Å and angles at copper atoms of 101.5 (2) and 78.5 (2)° as shown in Figure 1. Such an arrangement has been already found in the structure of $Cu_4[SC(NH_2)_2]_9(NO_3)_4$[3] where rectangles of copper atoms bridged by thiourea groups are connected by other thiourea groups to form an infinite chain. However, whereas two Cu–Cu distances are 2.707 (5) Å, the other distances are above 4 Å. As already noticed,[4] the copper–copper distances depend markedly on the nature of the bridging ligand. On each of the short sides of the parallelogram two copper atoms are bridged asymmetrically by one iodine atom (Cu–I = 2.512 (7) and Cu′–I = 2.632 (6) Å) whereas on each of the long sides they are bridged by a DPM molecule, with equal copper–phosphorus bond lengths (2.22 Å). In addition, each of the other two iodine atoms, above and below the plane of the parallelogram, bridges three metal atoms with distances Cu–I 2.721 (6), 2.737 (5), and 2.784 (5) Å, the distance with the fourth copper atom being 3.340 (6) Å. In our knowledge, a tricoordinate iodine atom is rather unusual, the resulting geometry being a distorted pyramid with the iodine atom at the apex and three copper atoms in the triangular basis. The Cu–I–Cu angles are 58.9, 68.7, and 83.6°. The Cu atom (see Figure 1) has a roughly trigonal coordination polyhedron (the sum of the angles around Cu is 350°) bonding one phosphorus and two iodine atoms, whereas Cu′ has a distorted tetrahedral geometry, bonding one phosphorus and three iodine atoms.[5] This result is similar to that found in other polynuclear complexes[6] possessing copper atoms with different geometries in the same compound.

Both P atoms have a distorted tetrahedral geometry (angles ranging from 104 to 119° and from 106 to 121° around P and P′, respectively) with expected values for the Cu–P bond lengths. The bite P–P′ is 3.08 (1) Å, the angle PCP′ being 113°.

The analogous chlorine derivative appears to be also dimeric from molecular weight measurements in chloroform and dichloroethane solutions and gives nonconducting solutions in dichloroethane.[1] These results suggest the compounds to have the same structure in the solid state and in solutions of slightly polar solvents. However, in solutions of appreciably polar solvents they undergo a dissociation in ionic species of lower molecular weight, in agreement with the values of the conductivity in acetone solutions.[7]

Acknowledgment. Support of this work by the C.N.R. is gratefully acknowledged.

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[3] R. G. Vranka and E L. Amma, *J. Amer. Chem. Soc.*, **88**, 4270 (1966).

[4] R. Mason, *et al.* (*J. Chem Soc., Chem. Commun.*, 446 (1972)) have recently reported a cluster of Cu(I) where four copper atoms are arranged in a distorted butterfly structure.

[5] Obviously the Cu–Cu bonding is not taken into account.

[6] J. M. Guss, R. Mason, K. M. Thomas, G. VanKoten, and J. G. Noltes, *J. Organometal. Chem.*, 40, C79 (1972); V. Albano, P. L. Bellon, G. Ciani, and M. Monassero, *J. Chem. Soc., Dalton Trans.*, 171 (1972), and references therein.

[7] A. Camus, private communication.

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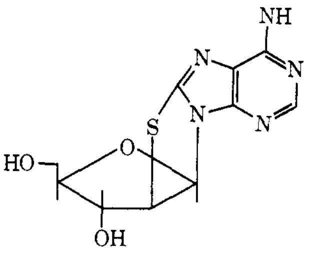
Received January 30, 1973

Synthesis of Cyclouridine Oligonucleotides Forming a Double Stranded Complex of Left-Handedness with Cycloadenosine Oligonucleotides

Sir:

Previously we have reported the synthesis and properties of single stranded oligonucleotides having 8,2′-*S*-cycloadenosine (A^s) (I).[1–3] It was found that these



I

oligomers had a left-handed stacked conformation despite their D-ribose backbone by criteria of nmr and CD and that they could not form double stranded complexes with poly (*U*). Since it was reported that L-ApA having left-handed stacking could form triple helical complexes with poly (U),[4] the cause of the failure to obtain complexes from A^spA^s and poly (U) has to be interpreted. In this communication, we report the synthesis of oligonucleotides containing 6,2′-anhydro-6-oxy-1-β-D-arabinofuranosyluracil (U^o) (II) and the formation of a double stranded complex of $(U^o)_8$ with $(A^s)_8$.

Starting from 1-β-D-arabinofuranosyl-5-bromouracil (III), compound II was obtained by an elegant method

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[1] M. Ikehara, S. Uesugi, and M. Yasumoto, *J. Amer. Chem. Soc.*, **92**, 4735 (1970); M. Ikehara and S. Uesugi, *ibid.*, **94**, 9189 (1972).

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[3] M. Ikehara, S. Uesugi, and J. Yano, *Nature (London), New Biol.*, **240**, 16 (1972).

[4] I. Tazawa, S. Tazawa, L. M. Stempel, and P. O. P. Ts'o, *Biochemistry*, **9**, 3499 (1970).