

**Figure 1.** Molecular structure of **4** with thermal ellipsoids constructed at the 30% probability level (except for H atoms). Bond lengths: Mo-I = 2.8225 (4), Mo-P2 = 2.4309 (12), Mo-C1 = 2.006 (4), Mo-O11 = 2.226 (3), Mo...P1 = 2.7234 (12), C1-P1 = 1.743 (4), P1-O11 = 1.512 (3) Å. Bond angles: O11-Mo-C1 = 73.4 (1)°, Mo-C1-P1 = 92.9 (2)°, C1-P1-O11 = 102.1 (2)°, P1-O11-Mo = 91.5 (1)°.

presence (GC-MS) of CHF<sub>3</sub> in the volatile reaction products.

The synthesis of **2** and **3** from an alkyldiyne represents a new approach to vinylalkylidene complexes whose chemistry is beginning to receive attention.<sup>9-13</sup> Previously molecules of this type have been obtained from reactions with acetylenes, and **2** and **3** represent the first examples of molybdenum complexes containing this ligand.

Elution with diethyl ether afforded the second product of the reaction between **1** and CF<sub>3</sub>I, a green crystalline compound (**4**) (35% yield). The analytical and NMR data<sup>14</sup> did not unambiguously define the structure of this molecule, and therefore an X-ray diffraction study<sup>15</sup> was undertaken.

(9) Stang, P. J. *Chem. Rev.* 1978, 78, 383-405.

(10) Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* 1978, 100, 7763-7765.

(11) Bruce, M. I.; Wallis, R. C. *J. Organomet. Chem.* 1978, 161, C1-C4.

(12) Adams, R. D.; Davison, A.; Selegue, J. P. *J. Am. Chem. Soc.* 1979, 101, 7232-7238.

(13) Følting, K.; Huffman, J. C.; Lewis, L. N.; Caulton, K. G. *Inorg. Chem.* 1979, 18, 3483-3486.

(14) Spectroscopic data for complex **4**: <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, room temperature)  $\tau$  5.12 (d, 5 H, C<sub>5</sub>H<sub>5</sub>,  $J_{\text{PH}} = 3$  Hz), 6.32 (d, 3 H, P(O)OMe,  $J_{\text{PH}} = 10$  Hz), 6.35 (d, 9 H, POMe,  $J_{\text{PH}} = 10$  Hz), 6.60 (d, 3 H, P(O)OMe,  $J_{\text{PH}} = 10$  Hz), 7.34 (ddd, 2 H, CH<sub>2</sub>Bu-*t*,  $J_{\text{HH}} = 14$ ,  $J_{\text{PH}} = 10$ ,  $J_{\text{PH}} = 6$  Hz), 9.04 (s, 9 H, Bu-*t*); <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>, room temperature)  $\delta$  30.7 (s, CMe<sub>3</sub>), 35.0 (s, CMe<sub>3</sub>), 51.2 (d, P(O)OMe,  $J_{\text{CP}} = 9$  Hz), 54.8 (d, POMe,  $J_{\text{CP}} = 8$  Hz), 57.9 (dd, CH<sub>2</sub>Bu-*t*,  $J_{\text{CP}} = 9$ ,  $J_{\text{CP}} = 9$  Hz), 94.5 (s, C<sub>5</sub>H<sub>5</sub>); <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, room temperature)  $\delta$  53.1 (d, P(O)OMe,  $J_{\text{PP}} = 27$  Hz), 176.4 (d, P(OMe)<sub>3</sub>,  $J_{\text{PP}} = 24$  Hz). The <sup>13</sup>C resonance due to the carbon Mo=C was not detected.

(15) Crystallographic data for complex **4**: Crystal data: C<sub>16</sub>H<sub>31</sub>IMoO<sub>6</sub>P<sub>2</sub>,  $M = 606.2$ , triclinic,  $a = 10.3130$  (16),  $b = 12.9811$  (3),  $c = 9.1912$  (18) Å,  $\alpha = 91.751$  (17)°,  $\beta = 106.166$  (15)°,  $\gamma = 94.981$  (16)°,  $V = 1175.4$  (4) Å<sup>3</sup>,  $\rho_{\text{obsd}} = 1.71$ ,  $Z = 2$ ,  $\rho_{\text{calc}} = 1.713$  g cm<sup>-3</sup>,  $\mu_{\text{(Mo K}\alpha\text{)}} = 18.9$  cm<sup>-1</sup>,  $F(000) = 600$  electrons, space group *P1* from *E* statistics and successful refinement. Of 5445 independent reflections measured on a Syntex P2, automated diffractometer (graphite monochromated Mo K $\alpha$  radiation and the  $\theta$ - $2\theta$  scan mode to a maximum  $2\theta$  of 55°), 4419 had  $I > 2.5 \sigma(I)$  and were used to solve (direct methods) and refine (full-matrix least-squares) the structure to  $R = 0.037$ ,  $P_w = 0.042$ , using the SHELX 76 programs.<sup>16</sup> All non-H atoms have been allowed anisotropic thermal motion, while all H atoms are set in idealized positions (at C-H = 1.08 Å) with  $U_{\text{H}} = 0.06$  Å<sup>2</sup> (C<sub>5</sub>H<sub>5</sub> and CH<sub>2</sub>) or  $U_{\text{H}} = 0.10$  Å<sup>2</sup> (CH<sub>3</sub>).<sup>17</sup>

(16) Scheldrick, G. M. University Chemical Laboratory, Cambridge, England, 1976.

(17) Complete crystallographic details will be published elsewhere. One referee has correctly pointed out that following Churchill, M. R. (*Inorg. Chem.* 1973, 12, 1213-1214), a more realistic representation of the electron density distribution would be given by a somewhat shorter C-H distance; however, a deficiency of the SHELX 76 system is that calculated hydrogen atoms are invariably set at C-H = 1.08 Å.

The molecular structure (Figure 1) illustrates that **4** is a molybdenum alkylidene complex containing a four-membered chelate ring Mo=C1-P1=O11. Molecular dimensions within this system may be compared to those of the Mn-C-P=O fragment in the compound [(NC)<sub>2</sub>C=CP(O)(OP*r*-*t*)<sub>2</sub>Mn(CO)<sub>2</sub>(diphos)].<sup>18</sup> Both rings are planar ( $\Sigma$ valence angles = 359.9 and 359.8°, respectively), with individual ring angles differing little between the two structures (maximum difference < 2°). Metal to ligand distances are naturally longer in the molybdenum system, but in the case of carbon this increase is somewhat offset by the alkylidene of the Mo=C link ( $\Delta_{\text{M-O}} = 0.069$  Å,  $\Delta_{\text{M-C}} = 0.049$  Å).

The  $\eta^5$ -C<sub>5</sub>H<sub>5</sub> ligand is oriented such that it is bisected by a plane constructed through Mo and P1 perpendicular to the chelate plane,<sup>19</sup> and the iodine and phosphite functions lie on the opposite side of the four-atom ring. The phosphite is cis to the alkylidene group, providing a steric rationale to the fact that the Bu-*t* group is found above (if I and P2 are below) the metallacyclic plane.

The formation of **4** is particularly interesting and represents an unusual transformation of an alkyldiyne into an alkylidene complex. The reaction involves an apparent Arbuzov reaction followed by migration of the phosphonate group from the molybdenum to the alkyldiyne carbon.

The chemistry and mechanism of formation of these molecules, which contain molybdenum carbon double bonds, are being investigated further.

**Acknowledgment.** We thank the S.R.C. for support.

**Supplementary Material Available:** Atomic positional and thermal parameters for alkylidene complex (**4** pages). Ordering information is given on any current masthead page.

(18) Newton, G. M.; Pantaleo, N. S.; King, R. B.; Diefenbach, S. P. *J. Chem. Soc., Chem. Commun.* 1979, 55-56.

(19) In C<sub>5</sub>H<sub>5</sub>ML<sub>2</sub> (alkylidene) complexes in which the alkylidene function is not constrained with a ring system, the complementary relative orientation of alkylidene and cyclopentadienyl fragments is found<sup>20</sup> and has recently been shown<sup>10,11</sup> to represent the minimum energy conformation of a relatively shallow potential well upon rotation.

(20) (a) Redhouse, A. D. *J. Organomet. Chem.* 1975, 99, C29-C30. (b) Hädicke, E.; Hoppe, W. *Acta Crystallogr., Sect. B* 1971, 27, 760-768.

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### Crystal Structure of a Tetranuclear Copper(II)-Inosine Monophosphate-*o*-Phenanthroline Complex: First Unambiguous Example of O<sub>6</sub> Coordination in a Metal-6-Oxopurine Complex

Sir:

The disputed existence of an N<sub>7</sub>-O<sub>6</sub> chelate from guanine to platinum has been the subject of a lively controversy among researchers studying the mechanism of action of antitumor platinum drugs.<sup>1,2</sup> Although some investigators feel that there

(1) (a) B. Rosenberg, *J. Clin. Hematol. Oncol.*, 7, 817 (1977); (b) D. M. L. Goodgame, I. Jeeves, F. L. Phillips, and A. C. Shapski, *Biochim. Biophys. Acta*, 378, 153 (1975); (c) M. M. Millard, J. P. Macquet, and T. Theophanides, *ibid.*, 402, 166 (1975); (d) J. Dehand and J. Jordanov, *J. Chem. Soc., Chem. Commun.*, 598 (1976); (e) J. P. Macquet and T. Theophanides, *Bioinorg. Chem.*, 5, 59 (1975); (f) G. Pneumatikakis, N. Hadjiliadis, and T. Theophanides, *Inorg. Chim. Acta*, 22, L1 (1977); (g) *Inorg. Chem.*, 17, 915 (1978).

Table I. Selected Distances (Å) in  $[\text{Cu}_4(5'-\text{IMPH}_{-1})_2(o\text{-phen})_4(\text{H}_2\text{O})_4]^{2+}[\text{NO}_3^-]_2 \cdot 14\text{H}_2\text{O}$ 

bond	fragment 1 <sup>a</sup>	fragment 2 <sup>a</sup>	bond	fragment 1 <sup>a</sup>	fragment 2 <sup>a</sup>
Cu <sub>1</sub> -O <sub>11</sub> (water)	2.196 (11)	2.169 (11)	N <sub>7</sub> -C <sub>5</sub>	1.358 (18)	1.361 (19)
Cu <sub>1</sub> -O <sub>6</sub>	1.959 (10)	1.953 (10)	N <sub>7</sub> -C <sub>8</sub>	1.315 (18)	1.314 (20)
Cu <sub>1</sub> -N <sub>11</sub> ( <i>o</i> -phen)	2.024 (12)	1.998 (12)	C <sub>8</sub> -N <sub>9</sub>	1.395 (19)	1.350 (21)
Cu <sub>1</sub> -N <sub>12</sub> ( <i>o</i> -phen)	2.020 (12)	2.002 (14)	N <sub>9</sub> -C <sub>4</sub>	1.317 (19)	1.359 (20)
Cu <sub>1</sub> -N <sub>7</sub>	2.013 (11)	2.020 (13)	N <sub>9</sub> -C <sub>1'</sub>	1.486 (23)	1.485 (21)
Cu <sub>3</sub> -O <sub>12</sub> (water)	2.222 (11)	2.235 (12)	C <sub>1'</sub> -O <sub>1'</sub>	1.397 (21)	1.364 (20)
Cu <sub>3</sub> -N <sub>13</sub> ( <i>o</i> -phen)	2.014 (14)	1.992 (14)	C <sub>1'</sub> -C <sub>2'</sub>	1.542 (24)	1.589 (28)
Cu <sub>3</sub> -N <sub>14</sub> ( <i>o</i> -phen)	2.005 (15)	2.030 (13)	C <sub>2'</sub> -O <sub>2'</sub>	1.380 (20)	1.437 (27)
Cu <sub>3</sub> -O <sub>8</sub> (phos)	1.949 (13)	1.929 (10)	C <sub>2'</sub> -C <sub>3'</sub>	1.515 (22)	1.415 (34)
Cu <sub>3</sub> -N <sub>1</sub>	2.019 (13)	2.001 (13)	C <sub>3'</sub> -O <sub>3'</sub>	1.475 (20)	1.410 (28)
N <sub>1</sub> -C <sub>6</sub>	1.379 (20)	1.394 (19)	C <sub>3'</sub> -C <sub>4'</sub>	1.521 (24)	1.570 (27)
N <sub>1</sub> -C <sub>2</sub>	1.301 (22)	1.376 (23)	C <sub>4'</sub> -O <sub>1'</sub>	1.412 (19)	1.445 (21)
C <sub>2</sub> -N <sub>3</sub>	1.363 (24)	1.384 (26)	C <sub>4'</sub> -C <sub>5'</sub>	1.508 (23)	1.454 (35)
N <sub>3</sub> -C <sub>4</sub>	1.388 (20)	1.385 (21)	C <sub>5'</sub> -O <sub>5'</sub>	1.434 (20)	1.419 (29)
C <sub>4</sub> -C <sub>5</sub>	1.394 (20)	1.359 (20)	P-O <sub>5'</sub>	1.586 (12)	1.594 (15)
C <sub>5</sub> -C <sub>6</sub>	1.454 (21)	1.444 (22)	P-O <sub>7</sub>	1.531 (12)	1.487 (14)
C <sub>6</sub> -O <sub>6</sub>	1.264 (18)	1.269 (18)	P-O <sub>8</sub>	1.534 (11)	1.512 (15)
			P-O <sub>9</sub>	1.487 (12)	1.474 (16)

<sup>a</sup> In this table the tetrameric cation is arbitrarily split into two halves. Fragment 1 is defined as 5'-IMP(1), *o*-phen(1), and the ligands around Cu<sub>1</sub> and Cu<sub>3</sub> (see Figure 1). Fragment 2 is defined as 5'-IMP(2), *o*-phen(2), and the ligands around atoms Cu<sub>2</sub> and Cu<sub>4</sub>.

is sufficient evidence to support the presence of such a chelate,<sup>1</sup> there is at present no crystallographic evidence for this mode of bonding among the many known structures of metal-guanine complexes.<sup>3,4</sup> The structure which comes closest to being described as an N<sub>7</sub>-O<sub>6</sub> chelate is that of a copper theophylline complex,<sup>5a</sup> in which a normal Cu-N<sub>7</sub> bond [1.956 (3) Å] is supplemented by a weak Cu...O<sub>6</sub> interaction taking place at a much longer distance [2.919 (3) Å].<sup>5b</sup> One of the key questions in the N<sub>7</sub>-O<sub>6</sub> controversy is whether O<sub>6</sub> is a viable metal-binding site or not. In this communication we report the structure of a complex which represents, to our knowledge, the first unambiguous example of metal-O<sub>6</sub> bonding.

Our work on the title compound,  $[\text{Cu}_4(5'-\text{IMPH}_{-1})_2(o\text{-phen})_4(\text{H}_2\text{O})_4]^{2+}[\text{NO}_3^-]_2 \cdot 14\text{H}_2\text{O}$ ,<sup>6</sup> is an extension of our earlier investigations<sup>7</sup> of ternary complexes, compounds consisting of a copper(II) ion, a nucleotide, and a  $\pi$ -aromatic base. The tetranuclear complex was prepared by mixing 10 mL of 0.02 M copper nitrate, 20 mL of 0.01 M disodium inosine monophosphate ( $\text{Na}_2(5'-\text{IMPH})$ ), and 20 mL of 0.01 M *o*-phenanthroline (*o*-phen).<sup>8</sup> The pH of the aqueous solution was adjusted with NaOH to 5.7–5.8.

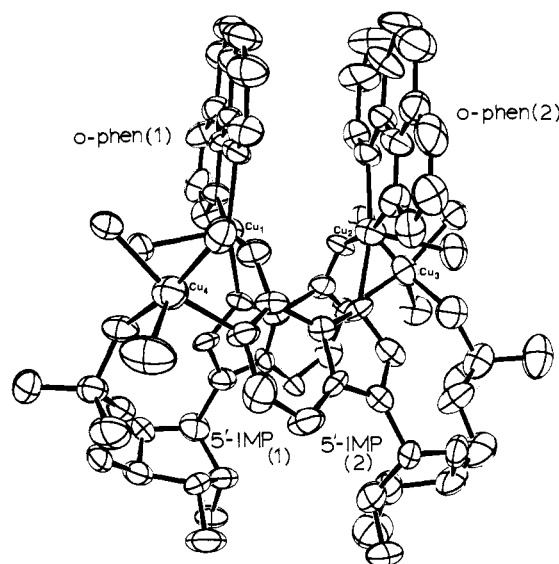


Figure 1. A molecular plot of the  $[\text{Cu}_4(5'-\text{IMPH}_{-1})_2(o\text{-phen})_4(\text{H}_2\text{O})_4]^{2+}$  cation, showing the square-pyramidal coordination around each copper atom. The C atoms of the *o*-phenanthroline groups around Cu<sub>3</sub> and Cu<sub>4</sub> have been removed for clarity.

(2) (a) G. Y. H. Chu and R. S. Tobias, *J. Am. Chem. Soc.*, **98**, 2641 (1976); (b) G. Y. H. Chu, S. Mansy, R. E. Duncan, and R. S. Tobias, *ibid.*, **100**, 593 (1978); (c) A. D. Kelman, H. J. Peresie, and P. J. Stone, *J. Clin. Hematol. Oncol.*, **7**, 440 (1977); (d) E. Sletten, *J. Chem. Soc., Chem. Commun.*, 558 (1971); (e) G. P. P. Kuntz and G. Kotowycz, *Biochemistry*, **14**, 4144 (1975); (f) R. B. Martin and Y. H. Mariam, in "Metal Ions in Biological Systems", Vol. 8, H. Sigel, Ed., Marcel Dekker, New York, 1979, Chapter 2.

(3) (a) D. J. Hodgson, *Prog. Inorg. Chem.*, **23**, 211 (1977); (b) V. Swaminathan and M. Sundaralingam, *CRC Crit. Rev. Biochem.*, **6**, 245 (1979); (c) R. W. Gellert and R. Bau in "Metal Ions in Biological Systems", Vol. 8, H. Sigel, Ed., Marcel Dekker, New York, Chapter 1, 1979; (d) B. de Castro, T. J. Kistenmacher, and L. G. Marzilli, *Agents Actions*, in press.

(4) However, in 6-thio-substituted purines this mode of bonding is well documented: an N<sub>7</sub>-S<sub>6</sub> chelate has been shown to exist in Pd(6-mercapto-9-benzylpurine)<sub>2</sub> [H. I. Heitner and S. J. Lippard, *Inorg. Chem.*, **13**, 815 (1974)].

(5) (a) D. J. Szalda, L. G. Marzilli, and T. J. Marzilli, and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **98**, 8371 (1976); (b) another example of a weak Cu...O<sub>6</sub> interaction [2.970 (2) Å] is found in a copper complex of 7,9-dimethylhypoxanthine [L. G. Marzilli, K. Wilkowski, C. C. Chiang, and T. J. Kistenmacher, *J. Am. Chem. Soc.*, **101**, 7504 (1979)]. However, in this case the metal-binding site is N<sub>1</sub>, and not N<sub>7</sub>.

(6) Abbreviations used in this work: 5'-IMPH<sub>-1</sub> represents the deprotonated form of 5'-IMP (5'-inosine monophosphate), deprotonated at N<sub>1</sub>; *o*-phen stands for *o*-phenanthroline (1,10-phenanthroline).

(7) (a) B. E. Fischer and R. Bau, *J. Chem. Soc., Chem. Commun.*, 272 (1977); *Inorg. Chem.*, **17**, 27–33 (1978); (b) C. Y. Wei, B. E. Fischer, and R. Bau, *J. Chem. Soc., Chem. Commun.*, 1053 (1978); (c) R. W. Gellert, B. E. Fischer, and R. Bau, *Biochem. Biophys. Res. Commun.*, **88**, 1443 (1979).

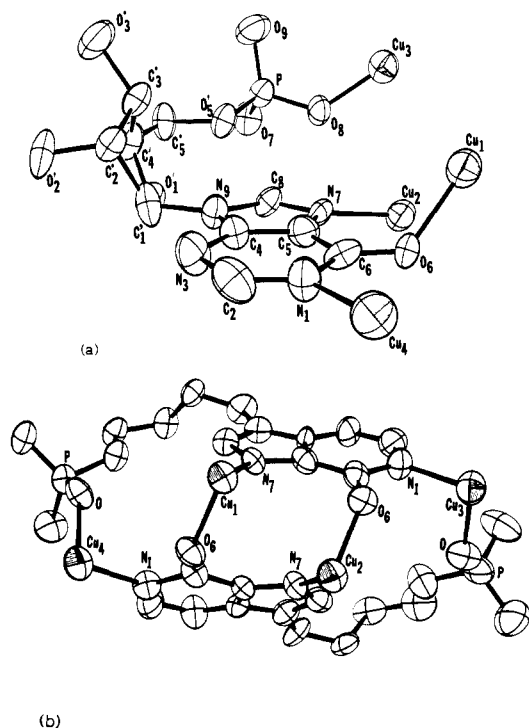
(8) This solution was prepared at a somewhat lower pH (about 5), due to the limited solubility of *o*-phen at higher pH values.

The resulting clear green solution was mechanically stirred at room temperature for 1 h. The reaction mixture (50 mL) was concentrated at reduced pressure to a final volume between 10 and 15 mL and was then set aside and allowed to evaporate. Dark green rectangular crystals appeared within 2 days.<sup>9</sup>

$[\text{Cu}_4(5'-\text{IMPH}_{-1})_2(o\text{-phen})_4(\text{H}_2\text{O})_4]^{2+}[\text{NO}_3^-]_2 \cdot 14\text{H}_2\text{O}$  crystallizes in the orthorhombic space group C22<sub>2</sub>1 with the following unit cell parameters:  $a = 18.823$  (6),  $b = 24.513$  (10),  $c = 40.253$  (20) Å,  $\rho(\text{calcd}) = 1.513 \text{ cm}^{-3}$  for  $Z = 8$ . Data were collected with monochromatic Cu K $\alpha$  radiation on a Syntex P2<sub>1</sub> diffractometer by the  $\theta/2\theta$  scan mode up to a  $2\theta$  (max) of 100°. The copper positions were located by direct methods.<sup>10</sup> A trial structure phased by these atomic positions, followed by a series of structure factor calculations and difference-Fourier syntheses, gradually revealed the rest of the molecule. Least-squares refinement of the structure yielded a final  $R$  value of 0.083 for 4598 nonzero reflections [ $I > 3\sigma(I)$ ].

(9) Vapor diffusion of the reaction mixture against *t*-BuOH yields similar crystals.

(10) MULTAN: A system of computer programs for the automatic solution of crystal structures from X-ray diffraction data [G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **A27**, 368 (1971)].



**Figure 2.** (a) A plot of one of the 5'-IMPH<sub>1</sub> ligands, showing its attachment to all four copper atoms. Note that the Cu atoms bonded to N<sub>1</sub> and N<sub>7</sub> are approximately coplanar with the purine ring, while that bonded to O<sub>6</sub> is markedly out of plane. This diagram also shows clearly the C<sub>3</sub>-endo puckering of the sugar ring. (b) The central core of the tetranuclear complex, viewed along its noncrystallographic twofold axis. Atoms C<sub>2</sub>, O<sub>2</sub>, C<sub>3</sub>, and O<sub>3</sub> of the ribose rings have been removed for clarity.

The structure of the [Cu<sub>4</sub>(5'-IMPH<sub>1</sub>)<sub>2</sub>(*o*-phen)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>]<sup>2+</sup> cation is shown in Figure 1 and selected distances are listed in Table I. A few other structural details are given in a footnote.<sup>11</sup> The copper atoms, as in other ternary complexes,<sup>7,12</sup> are in square-pyramidal environments. Each has a water ligand in an axial position and an *o*-phenanthroline chelate occupying two basal sites. The two remaining basal sites are N<sub>7</sub> and O<sub>6</sub> in the case of Cu<sub>1</sub> and Cu<sub>2</sub>, and N<sub>1</sub> and a phosphate oxygen atom in the case of Cu<sub>3</sub> and Cu<sub>4</sub>. Thus, each 5'-IMPH<sub>1</sub> ligand is coordinated to all four Cu atoms (Figure 2a) and is oriented in a direction opposite to the other (Figure 2b). A noncrystallographic twofold rotation axis passes through the midpoint of the Cu<sub>1</sub>-Cu<sub>2</sub> vector and is perpendicular to it. The two purine planes, incidentally, are inclined to each other at an angle of 47°.

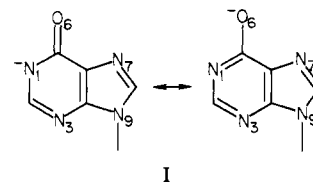
The Cu-O<sub>6</sub> distance [1.956 (10) Å] is unquestionably in the bonding range and is ~1 Å shorter than the weak Cu...O<sub>6</sub> interactions found previously.<sup>5</sup> The Cu-O<sub>6</sub>-C<sub>6</sub> angle of 126.1 (10)° corresponds to what one would expect for an sp<sup>2</sup>-hybridized O atom. It is interesting to note that, although the Cu atoms attached to N<sub>7</sub> and N<sub>1</sub> are roughly coplanar with the purine ring (average displacements of 0.38 and 0.03 Å, respectively), the Cu atom attached to O<sub>6</sub> is markedly out of plane (1.60 Å) (Figure 2a). This is also reflected by the Cu<sub>1</sub>-O<sub>6</sub>-C<sub>6</sub>-C<sub>5</sub> torsion angle (61.7°), which is a rough measure of the angle of inclination that the Cu-O<sub>6</sub> bond makes with the purine ring.

For coordination to a metal atom, the N<sub>1</sub> atom of the purine must of course be deprotonated, and this is consistent with the

(11) The angle at the deprotonated N<sub>1</sub> atom, C<sub>2</sub>-N<sub>1</sub>-C<sub>6</sub>, is 121(1)°. The orientation of the hypoxanthine base relative to the ribose sugar is anti [ $\chi$ -(C<sub>4</sub>-N<sub>9</sub>-C<sub>1</sub>-O<sub>1</sub>) = -165°, -167°]. The sugar rings are in the C<sub>3</sub>-endo puckering mode and the O<sub>3</sub>-C<sub>3'</sub> bonds relative to the sugar rings are gauche-gauche. A complete list of the torsion angles used to describe the conformation of the nucleotides, as well as all distances and angles in the molecule, are given in the Ph.D. dissertation of R. W. Gellert, University of Southern California, 1980.

(12) (a) K. Aoki, *J. Am. Chem. Soc.*, **100**, 7106 (1978); (b) *J. Chem. Soc., Chem. Commun.*, 589 (1979).

overall 2+ charge of the tetranuclear complex (four Cu<sup>2+</sup> ions plus two 5'-IMPH<sub>1</sub> molecules, each acting as a trinegative ligand). The ease with which N<sub>1</sub>-H becomes deprotonated when N<sub>7</sub> is attached to a metal atom is well-known.<sup>2a,b,13</sup> When deprotonated, the nucleophilicity of N<sub>1</sub> as well as O<sub>6</sub> is enhanced (as shown in I). In the present case, both sites become metalated.<sup>14</sup>



The infrared spectrum (KBr disk) of the title compound shows a band at ~1620 cm<sup>-1</sup>, in contrast to that of free 5'-IMP, which has an absorption at ~1675 cm<sup>-1</sup>. In the binuclear complex [Cu(5'-IMP)(dpa)(H<sub>2</sub>O)]<sub>2</sub>, which contains no metal-purine binding,<sup>7c</sup> the CO stretching vibration also has a high value (~1680 cm<sup>-1</sup>, KBr disk), characteristic of a free (uncomplexed) carbonyl group. The lowering of the CO stretching mode from ~1680 to ~1620 cm<sup>-1</sup> is often cited as evidence for the presence of N<sub>7</sub>-O<sub>6</sub> chelation.<sup>16,8</sup> Others, however, have argued that the phenomenon can be attributed to N<sub>1</sub> deprotonation.<sup>2a,b</sup>

In recent years there has been increasing speculation that N<sub>1</sub> deprotonation may have a bearing on the mechanism of action of antitumor platinum complexes.<sup>15,16</sup> Specifically, it is suspected to lead to base mispairing; this has been shown recently in a crystal structure determination of an unusual G-G base pair (again, with the G's coordinated to metal atoms through N<sub>7</sub>), in which the N<sub>1</sub> atom of one of the guanine rings is deprotonated.<sup>16</sup>

In summary, what we have here is an example of a 6-oxopurine ligand acting as an N<sub>7</sub>-O<sub>6</sub> bridge between two metal atoms rather than an N<sub>7</sub>-O<sub>6</sub> chelate to one metal atom. Our result neither supports nor refutes the existence of N<sub>7</sub>-O<sub>6</sub> chelates; however, it does show that metal-O<sub>6</sub> bonding is indeed feasible.<sup>17</sup> Finally, the N<sub>7</sub>-O<sub>6</sub> bridging structure found here (which had been suggested to exist in other compounds<sup>18</sup>) represents an alternative structural type which perhaps should be kept in mind when spectral evidence (used to argue for<sup>1</sup> or against<sup>2</sup> the N<sub>7</sub>-O<sub>6</sub> chelation mode) is evaluated.

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(13) H. Sigel, *J. Am. Chem. Soc.*, **97**, 3209 (1975).

(14) Binuclear binding from a deprotonated amide group is also found in complexes of thymine and its analogues [see J. K. Barton, D. J. Szalda, H. N. Rabinowitz, J. V. Waszczak, and S. J. Lippard, *J. Am. Chem. Soc.*, **101**, 1434 (1979); B. Lippert, D. Neugebauer, and U. Schubert, *Inorg. Chim. Acta*, **46**, L11 (1980); C. J. L. Lock, H. J. Peresie, B. Rosenberg, and G. Turner, *J. Am. Chem. Soc.*, **100**, 3371 (1978); B. Lippert and D. Neugebauer, *Inorg. Chim. Acta*, in press], and in complexes of cytosine, in which the ring amide is not protonated [e.g., L. G. Marzilli, T. J. Kistenmacher, and M. Rossi, *J. Am. Chem. Soc.*, **99**, 2797 (1977)].

(15) (a) B. Rosenberg, *Biochimie*, **60**, 859 (1978); (b) S. J. Lippard, *J. Clin. Hematol. Oncol.*, **7**, 453 (1977); (c) T. J. Kistenmacher, K. Wilkowski, B. de Castro, C. C. Chiang, and L. G. Marzilli, *Biochem. Biophys. Res. Commun.*, in press.

(16) Crystal structure determination of [Pt(NH<sub>3</sub>)<sub>2</sub>(9-EtGua)(1-Me-Cyt)<sup>2+</sup>][Pt(NH<sub>3</sub>)<sub>2</sub>(9-EtGuaH<sub>1</sub>)(1-MeCyt)<sup>+</sup>][ClO<sub>4</sub><sup>-</sup>]<sub>3</sub>; R. Faggiani, C. J. L. Lock, and B. Lippard, *J. Am. Chem. Soc.*, **102**, 5418 (1980).

(17) Other examples of metal binding to exocyclic carbonyl groups are known.<sup>14</sup> One example is the structure of a polymeric Mn/5'-CMP complex in which metal complexation from the cytosine ring takes place solely through the O<sub>2</sub> atom [K. Aoki, *J. Chem. Soc., Chem. Commun.*, 748 (1976)]. More recently, indirect evidence for Pt-O<sub>6</sub> binding has been found in a Pt-hypoxanthine complex [J. K. Barton, C. Caravana, and S. J. Lippard, *J. Am. Chem. Soc.*, **101**, 7269 (1979)].

(18) The possibility of an N<sub>7</sub>-O<sub>6</sub> fragment acting as a bridge between two metal atoms has previously been suggested in connection with polymeric platinum complexes found in solution (see Figure 14b of ref 2b) and in the solid state [N. Hadjiladis and T. Theophanides, *Inorg. Chim. Acta*, **16**, 77 (1976)].

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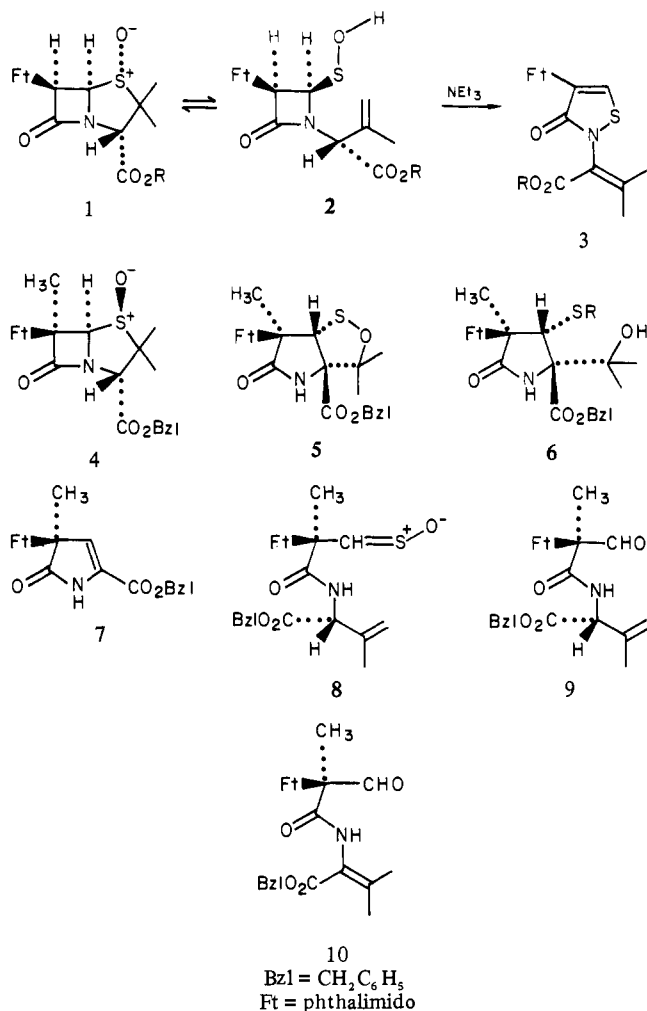
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**Rearrangement of Penicillin Sulfoxides in Base.  
Penicillin-Derived Sulfines**

Sir:

The abnormal Pummerer rearrangement of penicillin sulfoxides (1) provides, under acidic catalysis, methyl-substituted penams, cephams, and cephems as well as small amounts of isothiazolone-containing products.<sup>1</sup> The postulated sulfenic acid



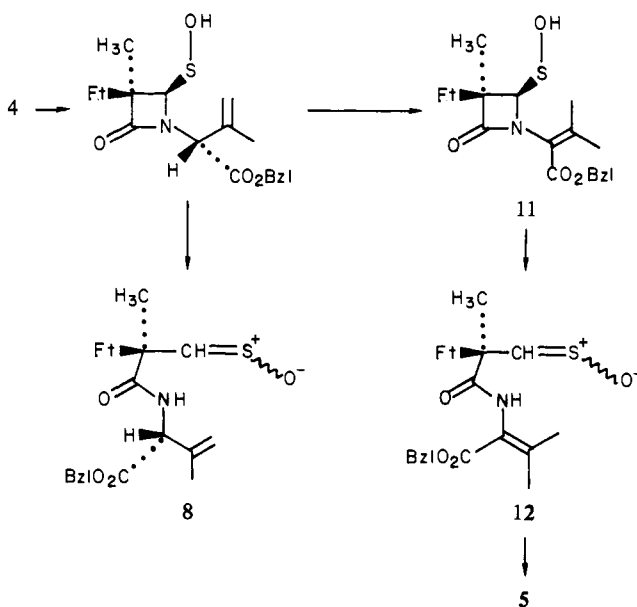
intermediate (2)<sup>1</sup> has since been isolated and shown to undergo clean base-catalyzed conversion to the isothiazolone (3).<sup>2</sup> In an attempt to determine the nature of the intermediates between 2 and 3,<sup>3</sup> we have examined the pyrolysis of a 6 $\alpha$ -methyl-substituted

(1) R. B. Morin, B. G. Jackson, R. A. Mueller, E. R. Lavagnino, W. B. Scanlon, and S. L. Andrews, *J. Am. Chem. Soc.*, **91**, 1401 (1969).

(2) T. S. Chou, J. R. Burgdorf, A. L. Ellis, S. R. Lammert, and S. P. Kukolja, *J. Am. Chem. Soc.*, **96**, 1609 (1974).

(3) Previously both sulfines and ene sulfenates have been suggested as intermediates in this transformation; cf. G. A. Koppel and S. Kukolja, *J. Chem. Soc., Chem. Commun.*, 57 (1975).

Scheme I



penicillin sulfoxide in basic media. In this substance (4) the absence of 6 $\alpha$ -hydrogen atom renders isothiazolone formation impossible. Thus, refluxing the  $\beta$ -sulfoxide 4<sup>4</sup> in pyridine (40 min, argon atmosphere) gave two new substances (total yield 65%) which were separated by flash chromatography<sup>5</sup> (benzene/ethyl acetate 3:1, silica gel). The slower moving component (5), mp 166–167 °C (from toluene),<sup>6</sup> was isomeric with the starting material, *m/e* 466, and showed no  $\beta$ -lactam absorption in the IR, but along with typical phthalimido and ester peaks (1790 and 1730 cm<sup>-1</sup>) exhibited a new amide absorption (1685 sh and 3430 cm<sup>-1</sup>). The NMR spectrum of 5 showed three methyl groups [<sup>1</sup>H (CDCl<sub>3</sub>)  $\delta$  1.27 (s, 3 H), 1.43 (s, 3 H), and 2.08 (s, 3 H); <sup>13</sup>C (CDCl<sub>3</sub>)  $\delta$  20.33, 21.89, 22.99 (q)]. The presence of a sulfenic ester moiety in 5 was demonstrated by instantaneous reaction with thiophenol to give the disulfide (6, R = SC<sub>6</sub>H<sub>5</sub>), 91%, mp 161.5–162.0 °C (from toluene), *m/e* 576, whereas triphenylphosphine gave, on subsequent hydrolysis of the first formed adduct, the hydroxy thiol (6, R = H), 64%, mp 205–220 °C dec (from ethyl acetate). At 230 °C this substance (6, R = H) lost H<sub>2</sub>S and acetone to yield the 4-pyrrolidin-2-one 7 [IR (CHCl<sub>3</sub>) 3440, 1780, 1725, 1685 (sh) cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.02 (s, 3 H), 5.27 (s, 2 H), 6.18 (d, *J* = 1.8 Hz, 1 H), 7.38 (s, 5 H), 7.51 (s, br, 1 H), 7.71–7.88 (m, 4 H); MS, *m/e* 376 (M<sup>+</sup>), 285, 147, 104, 91]. The relative stereochemistry was proven by X-ray analysis of 5 to be that shown.<sup>7</sup>

The faster moving component from the sulfoxide pyrolysis (8), *m/e* 466, also showed no  $\beta$ -lactam carbonyl but showed secondary amide bands, (1685 sh and 3430 cm<sup>-1</sup>) and in the NMR spectrum, the presence of an isopropenyl group adjacent to >CH-NH-CO [<sup>1</sup>H NMR (Z/E 8, CDCl<sub>3</sub>) 1.74 (s, br, 3 H), 4.99–5.09 (m, 3 H), 7.41 (d, br, *J* = 7 Hz, 1 H)]. The sulfine hydrogen was clearly visible at 8.69 and 8.76 (*Z/E* ratio = 80:20). These values are essentially identical with those reported for the stereoisomeric propanethial S-oxides, the lachrymatory principal of onions.<sup>8</sup> The masked aldehyde functionality in 8 was exposed on mild acid

(4) J. E. Baldwin, S. R. Herchen, J. C. Clardy, K. Hirotsu, and T. S. Chou, *J. Org. Chem.*, **43**, 1342 (1978).

(5) W. C. Still, M. Kahn, and A. Mitra, *J. Org. Chem.*, **43**, 2923 (1978).

(6) All new crystalline compounds have satisfactory analytical and spectral data.

(7) The crystallographic data for 5 were as follows: *a* = 13.088 (1) Å, *b* = 12.803 (1) Å, *c* = 16.325 (2) Å,  $\beta$  = 110.70 (1)°; monoclinic, space group P2<sub>1</sub>, *Z* = 4. The crystal contained some disordered chloroform which severely degraded the refinement. The formula is approximately C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>S·0.25 CHCl<sub>3</sub>. The measured density is 1.30 g cm<sup>-3</sup>. The density calculated from this formula is 1.29 g cm<sup>-3</sup>.

(8) E. Block, L. K. Revelle, and A. A. Bazzi, *Tetrahedron Lett.*, 1277 (1980).