Molecular Structure of Dimeric Magnesium Phenyl Phosphatosulfate

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Introduction

The X-ray crystal structures have been reported for magnesium ion complexes of adenosine 5′-triphosphate (ATP)[1] as well as magnesium pyrophosphate.[2] The ATP substrate provides the function of dephosphorylation or phosphoryl group transfer. However there are no X-ray structural studies on the Mg^{2+} complexes of phosphatosulfate ester having sulfate group as well as phosphate group: their substrates act as a mediator for biological sulfate transfer.[3,4]

This paper reports the molecular structure of magnesium phenyl phosphatosulfate as a model complex for the above mediator. We will demonstrate the conformation of ligands around the magnesium center and the differences between the chemical bonds of phosphate group−Mg^{2+} and sulfate group−Mg^{2+}.

Experimental Section

Preparation of Complex. The synthesis of phenyl phosphatosulfate ester (PPSE) used in this work was prepared according to the literature method.[5,6] The colorless crystal of the title compound (**1**) was prepared by adding ether to the *N*,*N*-dimethylformamide (DMF) solution of PPSE (20 mM) and $MgCl_2$ (60 mM) and by keeping it at room temperature for at least 2 weeks.

Single-Crystal X-ray Structure Analysis. Since crystals were damaged rapidly in air, a single crystal was sealed into an X-ray capillary tube and was used for the X-ray experiment.[7] A rapid data-collection system (MAC Science DIP100 using a Fuji Imaging Plate as an X-ray detector)[8] was used to measure the intensity data to minimize the radiation damage. The structure was solved by the Monte Carlo−MULTAN method.[9]

Details of data collection and refinement parameters are presented in Table 1. The coordinates and the equivalent isotropic thermal parameters[10] are listed in Table 2.

Table 1. Crystallographic Data for MgPPS·4DMF

chem formula: $C_{18}H_{33}O_{11}N_4PSMg$	fw = 568.82
a = 12.076(6) Å	space group: $P\bar{1}$
b = 11.208(5) Å	T = 20 °C
c = 18.266(10) Å	λ = 0.710 69 Å
α = 38.33(2)°	ρ_{calc} = 1.376 g cm^{-3}
β = 89.19(2)°	μ = 2.615 cm^{-1}
γ = 73.33(3)°	$R(F_o)^a$ = 0.0871
V = 1373.1 Å^3	
Z = 2	

[a] $R(F_o) = \sum_h||F_o| - |F_c||/\sum_h|F_o|$.

Table 2. Final Atomic Coordinates (Å) and Equivalent Isotropic Thermal Parameters (Å^2) with ESD's in Parentheses

atom	x	y	z	B_{eq}[a]
Mg(1)	−0.4220(2)	0.2994(4)	−0.1602(2)	3.0(5)
S(1)	−0.3827(2)	0.0091(3)	−0.1736(2)	3.2(4)
P(1)	−0.3402(2)	−0.2182(3)	0.0753(2)	2.6(3)
O(1)	−0.1941(4)	−0.3508(9)	0.1316(5)	3.6(10)
O(2)	−0.3964(4)	−0.3537(8)	0.1695(5)	3.2(10)
O(3)	−0.3580(5)	−0.0200(8)	0.0186(5)	3.2(10)
O(4)	−0.3850(5)	−0.1710(8)	−0.0309(5)	3.2(10)
O(5)	−0.4178(5)	0.2016(9)	−0.2226(5)	3.7(11)
O(6)	−0.2589(5)	−0.0783(11)	−0.1598(6)	4.9(14)
O(7)	−0.4732(6)	0.0234(11)	−0.2325(6)	4.8(14)
O(8)	−0.4885(6)	0.6120(9)	−0.3463(6)	4.4(12)
O(9)	−0.2433(5)	0.2767(11)	−0.1660(6)	4.6(14)
O(10)	−0.4021(5)	0.3828(9)	−0.0941(6)	4.0(13)
O(11)	−0.8393(15)	0.356(2)	−0.4938(14)	15(5)
N(1)	−0.6264(8)	0.9620(13)	−0.5203(8)	5.2(17)
N(2)	−0.0530(6)	0.1605(13)	−0.1602(8)	5(2)
N(3)	−0.3421(6)	0.3127(12)	0.0570(8)	4.4(17)
N(4)	−0.7541(9)	0.4752(16)	−0.4681(9)	7(3)
C(1)	−0.1275(7)	−0.5516(13)	0.1931(8)	3.6(17)
C(2)	−0.1343(9)	−0.7351(15)	0.3083(10)	5(2)
C(3)	−0.0597(11)	−0.9328(18)	0.3671(12)	7(3)
C(4)	0.0181(10)	−0.945(2)	0.3167(12)	7(3)
C(5)	0.0236(9)	−0.758(2)	0.2018(12)	7(3)
C(6)	−0.0508(8)	−0.5535(17)	0.1366(10)	5(2)
C(7)	−0.5726(9)	0.7697(15)	−0.3944(9)	5(2)
C(8)	−0.5895(15)	0.996(3)	−0.6101(13)	9(4)
C(9)	−0.7243(12)	1.144(2)	−0.5696(15)	9(3)
C(10)	−0.1601(7)	0.1537(15)	−0.1480(9)	4(2)
C(11)	−0.0259(10)	0.318(2)	−0.1988(12)	6(3)
C(12)	0.0406(11)	0.015(3)	−0.1410(16)	8(4)
C(13)	−0.3863(7)	0.2725(14)	0.0157(9)	3.8(18)
C(14)	−0.3052(12)	0.4890(2)	−0.0261(12)	7(3)
C(15)	−0.3311(11)	0.182(2)	0.1859(11)	7(3)
C(16)	−0.750(2)	0.445(4)	−0.5220(18)	17(6)
C(17)	−0.795(2)	0.418(3)	−0.3786(16)	14(5)
C(18)	−0.6657(15)	0.573(3)	−0.5102(17)	15(5)

[a] $B_{eq} = {}^4/_3(\sum_i\sum_j \mathbf{B}_{ij}a_ia_j)$

Results and Discussion

The structural unit consists of the two anions of phenyl phosphatosulfate ester (PPS^{2-}) and two cations of Mg^{2+}, and eight DMFs. The structure of complexed dimeric molecule formulated as $(MgPPS\cdot4DMF)_2$ is shown in Figure 1 with the atom numbering scheme. The interatomic distances and angles given in Table 3 describe the coordination geometry of the ligands around Mg^{2+}. In the dimeric unit, there exists a center of symmetry between the two subunits formulated as MgPPS·-4DMF.

In the metal complex of ATP, Mg^{2+} is located in the center of an octahedral coordination geometry established by the nonbridging oxygen atoms in α, β, and γ phosphate groups.[1] The octahedral coordination geometry of oxygen atoms around each Mg^{2+} in the structural unit of $(MgPPS\cdot4DMF)_2$ indicates the following features. (1) An anion of PPS^{2-} interacts with a magnesium center via the nonbridging oxygen atoms in the

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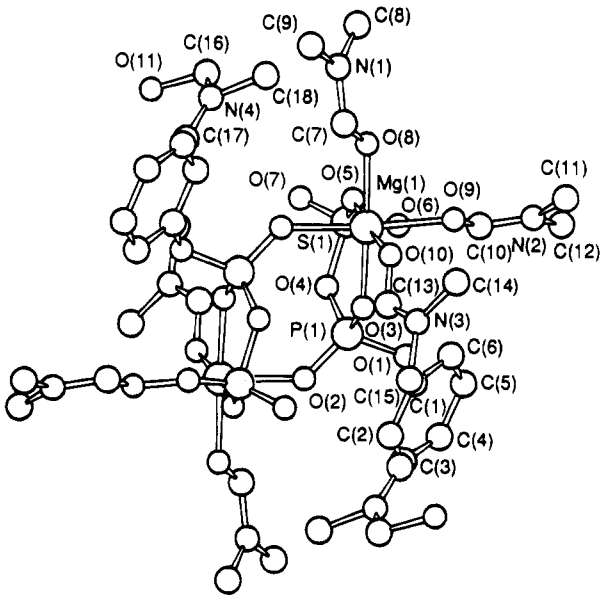


Figure 1. Perspective view of molecular structure of $(MgPPS \cdot 4DMF)_2$ with atom numbering scheme.

Table 3. Selected Bond Lengths (Å) and Bond Angles (°) with Atomic Labeling

P(1)−O(1)	1.590(11)	Mg(1)−O(3)	2.054(10)
P(1)−O(2)	1.479(10)	Mg(1)−O(5)	2.104(11)
P(1)−O(3)	1.475(10)	Mg(1)−O(8)	2.063(12)
P(1)−O(4)	1.609(10)	Mg(1)−O(9)	2.111(13)
S(1)−O(4)	1.626(10)	Mg(1)−O(10)	2.074(12)
S(1)−O(5)	1.446(10)	Mg(1)−O(2)[a]	2.071(10)
S(1)−O(6)	1.429(12)		
S(1)−O(7)	1.429(13)		

O(3)−Mg(1)−O(5)	85.7(4)	O(8)−Mg(1)−O(10)	92.6(5)
O(3)−Mg(1)−O(9)	94.0(5)	O(8)−Mg(1)−O(2)[a]	88.1(4)
O(3)−Mg(1)−O(10)	93.1(4)	O(9)−Mg(1)−O(10)	84.3(5)
O(3)−Mg(1)−O(2)[a]	91.5(4)	O(3)−P(1)−O(4)	111.6(5)
O(3)−Mg(1)−O(8)	88.7(4)	P(1)−O(4)−S(1)	129.5(6)
O(5)−Mg(1)−O(9)	88.6(5)	O(4)−S(1)−O(5)	105.7(6)
O(5)−Mg(1)−O(2)[a]	93.3(4)	S(1)−O(5)−Mg(1)	140.7(7)
O(8)−Mg(1)−O(9)	86.7(5)		

[a] O atom of the next PPS^{2-}.

phosphate and sulfate groups: the nature of the chemical bond with bidentate manner is ionic between Mg^{2+} and the above oxygen atoms from a point of view of the magnitude (ca. 2.1 Å) of bond lengths between them. (2) Another PPS^{2-} interacts with the same magnesium center via a nonbridging oxygen atom in phosphate group. (3) The three DMF molecules interact via each oxygen atom in their own aldehydro groups. Since the six nearest neighbour distances of Mg···O range from 2.054-(10) to 2.104(11) Å (see Table 3) and coincide with the sum, 2.05 Å of their ionic radii, the interaction of Mg···O is characteristic of an ionic bond. The remainding parts of the two DMFs do not interact with Mg^{2+} since $r(O(11)\cdots Mg^{2+})$ = 7.48 Å. The conformation about the axis of the S−O−P bond shows the so-called "eclipsed" conformer, as shown in Figure 2. On the other hand, the "staggered" conformation about the P−O−P and P−O−P−O−P bonds is well known in the crystalline phase of the pyrophosphate or triphosphate compound.[2,11,12]

Packing among the structural units formulated as $(MgPPS \cdot 4DMF)_2$ may be controlled by week intermolecular interaction between nitrogen atom in a DMF molecule and methyl group in another DMF molecule as shown by the eight arrows in Figure 3. The week intermolecular interaction among the above structural units brings about their linear linkages. The two phenyl groups in a dimeric molecule face toward each phenyl

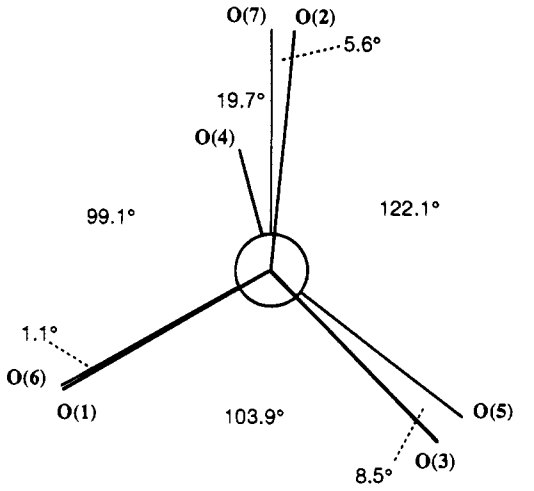


Figure 2. Torsion angles about the axis of the S−O−P bond, as shown in the form of Newmann projections.

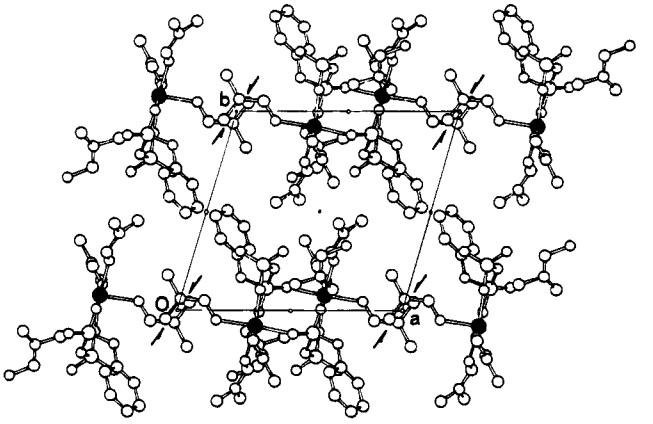
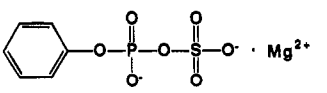


Figure 3. Molecular packing projected on the ab plane. The solid circles show the magnesium ions.

group which belongs to another upper and lower linkages, respectively: the much more week interaction among the linkages may be controlled by the London dispersion forces.

Figure 1 shows all the nonbridging oxygen atoms in phosphate group binds Mg^{2+}, but only an oxygen atom O(5) in sulfate group binds Mg^{2+}. Since the distances between O(6) or O(7) in sulfate group and Mg^{2+} are equal to 4.12 and 3.39Å, respectively, Mg^{2+} are not bound to O(6,7). Thus, Mg^{2+} preferrs the phosphate group to the sulfate group via their nonbridging oxygen atoms. The phosphatosulfate ester associated with Mg^{2+} may act as a mediator for biological sulfate transfer: Mg^{2+} can play the role of the catalytic activity for the reactions of the cleavage of the ester bond as well as the sulfate-transfer.[3,4] Since the ATP−sulfurylase is capable of forming adenylyl sulfate (APS) from ATP and sulfate under the requirement of Mg^{2+}, the modeling compound of APS should be considered as the title compound (**1**).



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Here, the substrate of APS is reduced to sulfite under the government of APS reductase.

Supporting Information Available: Tables of experimental details and refinement parameters, thermal parameters, rectangular coordinates and lists of atomic distances and angles (9 pages). Ordering information is given on any current masthead page.

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