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A Spirobicyclic Complex of Schmidpeter's Ligand, Bis(tetraphenylimidodiphosphinato) beryllium, $Be(OPh_2PNPPh_2O)_2$, an Inorganic Analog of Beryllium bis(β-diketonates)

Ionel Haiduc,[1] Julio Zukerman-Schpector,[2] Eduardo Castellano,[3] and Raymundo Cea-Olivares[4]

[1]Facultatea de Chimie, Universitatea "Babes-Bolyai" Cluj-Napoca, Romania

[2]Departamento de Quimica, Laboratorio de Cristalografia, Universidade Federal de Sao Carlos, Sao Carlos, Brazil

[3]Departamento de Fisica, Universidade Federal de Sao Carlos, Sao Carlos, Brazil

[4]Instituto de Quimica, Universidad Nacional Autonoma de Mexico, Ciudad Universitaria, 04510 Mexico D.F., Mexico

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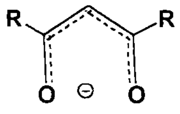
ABSTRACT: *The crystal structure of bis(tetraphenylimidodiphosphinato)beryllium (as a benzene solvate),* $Be(OPh_2PNPPh_2O)_2 . C_6H_6$, was determined by X-ray diffraction and compared with that of beryllium acetylacetonate, $Be(OCMeCHCMeO)_2$. The imidodiphosphinate is an inorganic spirobicyclic system, $Be(OPNPO)_2$, with tetrahedrally coordinated beryllium. Unlike the planar BeO_2C_3 rings in the acetylacetonate, the two six-membered BeO_2P_2N inorganic rings are nonplanar and display a skew boat conformation. © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:244–248, 2000

INTRODUCTION

The chemistry of metal chelates is dominated by organic ring-forming ligands, among which deprotonated enolic forms of *β*-diketones (**1**) are some of the most versatile and have been much investigated [1]. In the sixties, Alfred Schmidpeter introduced a new class of ligands, dichalcogenoimidodiphosphinates, **2** and **3** [2], which form inorganic (carbon-free) chelate rings [3]. These proved to be extremely versatile and have been extensively used. In recent years a renewed interest for this class of ligands and their complexes is observed, and they have been extensively used in our laboratory [4] and in others [5–7].



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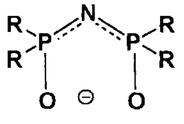

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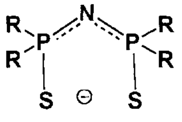

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The analogy between *β*-diketonato complexes **4** and dichalcogeno imidodiphosphinato complexes **5** is

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Correspondence to: Ionel Haiduc and Eduardo Castellano.

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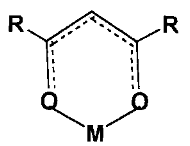
Dedicated to Alfred Schmidpeter on the occasion of his 70th birthday and in recognition of his discovery of the versatile dichalcogenoimidodiphosphinate ligands.

only formal, since the sp^2 hybridization of carbon in the organic chelate ring imposes planarity, whereas the sp^3 hybridization of phosphorus in the inorganic chelate rings allows for much more flexibility, and these metallocycles exhibit a broad variety of conformations, well documented by X-ray diffraction studies (for reviews see Ref. [7]).



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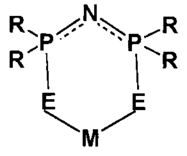
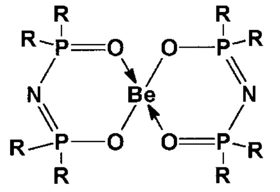


E = O, S, S

5

The beryllium compound, $Be(OPh_2PNPPh_2O)_2$, has been previously prepared from beryllium bis(acetylacetonate), $Be(acac)_2$, and tetraphenylimidodiphosphinic acid, OPh_2PNPPh_2OH, at 110°C (without solvent) and a spirobicyclic structure **6**, R = Ph, has been suggested on the basis of analytical and spectroscopic evidence [8].



6

The molecular structure of beryllium acetylacetonate is well known from X-ray diffraction studies both at room temperature [9] and at 119K (a more accurate determination) [10] and from an electron diffraction investigation [11]. In view of our interest in inorganic (carbon-free) chelate rings [3], we considered it useful to determine the crystal structure of bis(tetraphenylimidodiphosphinato)beryllium and to compare the molecular structures of the two compounds.

RESULTS AND DISCUSSION

Bis(tetraphenylimidodiphosphinato)beryllium, $Be(OPh_2PNPPh_2O)_2$, was prepared by a modification of the published method [8], by refluxing beryllium acetylacetonate, $Be(acac)_2$, with tetraphenylimidodiphosphinic acid, OPh_2PNPPh_2OH, in benzene. Alternatively, the compound was also obtained from beryllium(II) chloride in aqueous solution and the potassium salt of the ligand in ethanol. Crystals suitable for X-ray analysis were obtained by maintaining a benzene solution of the compound in a refrigerator (ca. −5°C) for several weeks.

A ZORTEP drawing of the molecular structure, with the atom numbering scheme, is shown in Figure 1, and selected interatomic distances and bond angles are listed in Table 1.

The molecule contains a tetrahedrally coordinated beryllium atom as the coordination center of a spirobicyclic system. The beryllium atom sits on a twofold crystallographic axis. The two six-membered BeO_2P_2N inorganic rings are nonplanar and display a skew boat conformation, but the deviations from planarity are small. In the rings, the Be–O bond lengths seem to differ slightly, but the P–N bonds and

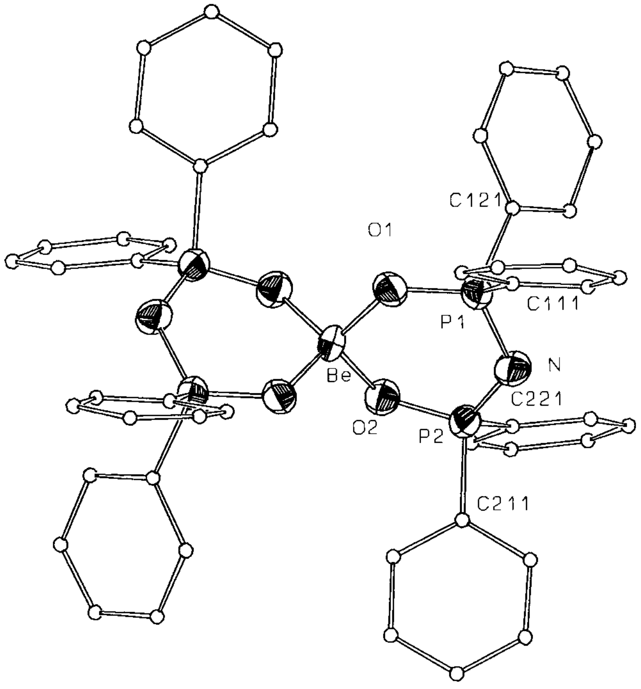


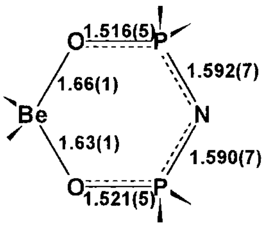
FIGURE 1

TABLE 1 Important Bond Lengths (Å) and Angles (°) in $Be(OPh_2PNPPh_2O)_2$

Be–O(1)	1.66(1)
Be–O(2)	1.63(1)
P(1)–N	1.592(7)
P(2)–N	1.590(7)
P(1)–O(1)	1.516(5)
P(2)–O(2)	1.521(5)
O(1)–Be–O(2)	108.5(6)
O(1)–Be–O(1)′	108.1(5)
O(2)–Be–O(2)′	109.3(6)
O(1)–Be–O(2)′	111.3(6)
Be–O(1)–P(1)	126.0(4)
Be–O(2)–P(2)	125.6(4)
P(1)–N–P(2)	120.9(4)
N–P(1)–O(1)	116.0(3)
N–P(2)–O(2)	116.2(3)

the P–O bonds are identical, within the limits of the standard deviations. In the acetylacetonate, $Be(acac)_2$, the Be–O bond lengths are somewhat shorter (range 1.614 to 1.623 A). The O-Be-O angles in the imidodiphosphinate are tetrahedral, with small deviations from the ideal value. To the best of our knowledge a similar beryllium diketonato complex with phenyl groups instead of methyls, another attractive compound for comparison, has not been structurally characterized.

The interatomic distances within the BeO_2P_2N six-membered ring suggest a π-electron delocalization, as shown in **7**, similar to that observed in the acetylacetonate analogue **8**.



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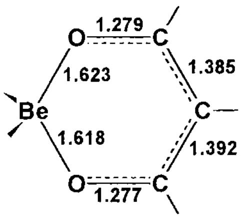
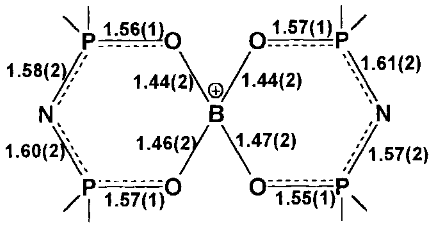
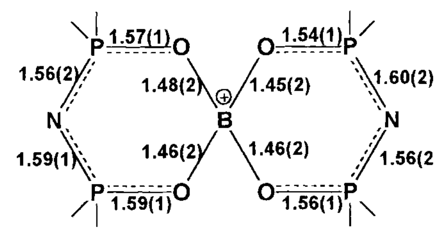


8

The orientation of phenyl substitutents also deserves a comment. Thus, in $Be(OPh_2PNPPh_2O)_2$ in each chelate ring two phenyl groups (one at each phosphorus atom) are in equatorial positions, nearly coplanar with the inorganic ring skeleton, while the other two display axial orientation, trans to each other, that is, on opposite sides of the inorganic ring (Figure 1).



9a



9b

A boron-containing cationic compound (two independent molecules **9a** and **9b**), isoelectronic with **6** (R = Ph) has also been structurally characterized [5g].

Surprisingly, the boron-oxygen bonds are shorter than the beryllium-oxygen bonds, and the phosphorus-oxygen bonds are slightly longer in the boron compound than in the beryllium compound. There are only minor differences in the values of the bond angles in the BeO_2P_2N and BO_2P_2N rings (O-Be-O 108.5° vs. O-B-O 111°; P-N-P 120° in both compounds).

EXPERIMENTAL

Preparation of $Be(OPh_2PNPPh_2O)_2$

A solution containing 0.208 g (1 mmol) of beryllium acetylacetonate, $Be(acac)_2$, and 0.840 g (2 mmol) tetraphenylimidodiphosphinic acid, OPh_2PNPPh_2OH, in 25 mL of anhydrous benzene was refluxed for 6.5 hours. Concentration of the solution caused a white solid, m.p. 220–221°C (benzene solvate, lit. m.p. 221–222°C) to be deposited [8].

Beryllium(II) chloride (0.087 g, 1.1 mmol) was dissolved in water (5 mL) and added to an ethanolic solution containing 1.002 g (2.2 mmol) of potassium tetraphenylimidodiphosphinate, $K[OPh_2PNPPh_2O]$, under stirring. The resulting mixture, containing a colorless solid, was stirred for 45 minutes and the product was filtered off, washed with water, and ethanol, and dried in air (m.p. 237°C, unsolvated; lit. m.p. 237°C) [8].

^{31}P NMR spectrum (δ, relative to 85% H_3PO_4): 28.26 ppm (in $CDCl_3$); lit. 27.22 ppm (in benzene) [8].
IR spectrum (KBr pellets, cm^{-1}): 1468w, 1455w, 1435s, 1192m(νPN), 1170m, 1120s(νPO), 778m, 756m, 722s, 692s(νPC_2).
Mass spectrum (EI, *m/e*, % relative intensity, assignment): 840(2.3) M^+-H, 763 (1.9) M-Ph, 426 (2.1) $BeO_2NHP_2Ph_4$, 417 (61) $Ph_4P_2O_2NH$, 416 (100) $Ph_4P_2O_2N$, 201 (54) Ph_2PO, 77 (98) Ph.

Crystal Structure Determination

The data were collected on a CAD-4 diffractometer, in the $\omega/2\theta$ scan mode with ω scan width = $0.80 + 0.35\tan\theta$, using graphite monochromated Mo Kα radiation. The data were corrected for Lorenz and polarization effects but not for absorption. The structure was solved by direct methods followed by normal difference Fourier techniques. Refinement was carried out by blocked-matrix least squares. The programs used were: SHELX86 [12], SHELX76 [13], and ZORTEP [14]. Scattering factors for non-hydrogen atoms were from Ref. [15], and corrections for

TABLE 2 Deviations from the mean plane[a]

Atom	*Distance* (*Å*)
Be	−0.11(1)
N	−0.107(7)
P(1)	0.153(2)
P(2)	−0.062(2)
O(1)	−0.050(5)
O(2)	0.176(5)

[a] The puckering coordinates [18] are: $q^2 = 1.496(6)$A, $\theta = 90.8(2)$ graus; $q^3 = -0.202(6)$ A, $\phi = 218.8(2)$ graus; $Q = 1.496(6)$ A

anomalous dispersion from Ref. [16] and for H-atoms from Ref. [17]. Hydrogen atoms were included, as a fixed contribution, on stereochemical grounds with an overall isotropic temperature factor that refined to 0.120(9) A^2. Details about the structure determination are collected in Table 2.

A crystallization benzene molecule, sitting on a two-fold axis, was found to be disordered. A difference map indicated, however, that the disorder could be satisfactorily described by a simple model postulating two different orientations; the atoms in the two possible positions were treated in the refinement with the occupation factor constrained to a sum of one, with a common temperature factor for all disordered atoms; no constraints were imposed to the two atoms on the two-fold axis. The refinement converged to reasonable occupation values of 0.428 and 0.572 for the two orientations. The rather poor final agreement factor is due to the disordered nature of the structure.

Regarding the nonplanarity of the six-membered BeO_2P_2N ring, a calculation of the mean plane was performed; all the six atoms were included. Also the Cremer and Pople puckering parameters [18] were determined showing that the ring is in a twisted-boat conformation (See Table 3).

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