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Synthesis and crystal structures of new potential chelating sulfonylamidophosphate ligands

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ABSTRACT

Sulfonylamidophosphates with formula $PhSO_2NHP(O)(OR)_2$ (H**L1**: R = $PhCH_2$—; H**L2**: R = *p*-MeC_6H_4—) and $(p\text{-}C_6H_4SO_2NHP(O)(OMe)_2)_2$ (H_2**L3**) were synthesized *via* a three-step procedure based on Kirsanov reaction. Sodium salts Na**L1**, Na**L2** and Na_2**L3** were prepared from the corresponding sulfonylamidophosphates to explore their acid nature of the imide nitrogen. The products were characterized by means of ^1H, ^{31}P NMR and IR spectroscopies and elemental analysis. Crystal structures of H**L2**, H_2**L3** and Na**L2** were determined using X-ray crystallography. H**L2** produces a dimeric aggregate *via* intermolecular hydrogen bonding. In contrast, H_2**L3** and Na**L2** form 1D polymeric chains.

1. Introduction

The investigations of β-diketones and their derivatives include different branches of the chemical science, among others the organic, coordination, bio- and theoretical chemistry. Much interest is attracted to carbacylamidophosphates, containing functional fragment C(O)NHP(O), because of their properties as extractants [1–3], urease inhibitors [4], enzyme inhibitors [5,6], antivirus [7] and anticancer activity [8,9]. The presence of the phosphoryl group possessing high affinity to high charged metallic ions, allows to use this type of compounds in coordination chemistry of lanthanides and actinides [10–13].

Many efforts have been devoted to the synthesis of another type of structural analogs of β-diketones–sulfonylamidophosphates with the structural fragment $S(O)_2NHP(O)$. This type of compounds was first synthesized by Kirsanov [14] and used as bactericidal agents in medicine and toxicology [15], while some of them are used as pesticides [16]. In addition, these compounds are potentially bidentate O,O-donor chelating ligands for metal ions. However, the data on these compounds and their coordination properties as well as their potential use are scarce today. Recently, we reported the preparation and study of the coordination properties of one of the representatives of sulfonylamidophosphates the compound dimethyl(phenylsulfonyl)amidophosphate [$PhSO_2NHP(O)(OMe)_2$] (Scheme 1, at the top) [17,18] and particularly the photophysical properties of a new series of NIR emitting lanthanide complexes were described [19,20]. It was shown that the determined decay time for ytterbium compound with the ligand $PhSO_2NHP(O)(OMe)_2$ is one of the longest among known for the solid state Yb^{III} complexes with organic ligands. The interest in this topic is caused by the wide range of application of lanthanide-based systems with β-diketones and their derivatives in bioanalytical assays, diagnostic researches, drug discoveries, laser emission and imaging techniques [21–25]. It is expected that depending on the nature of substituents attached to the phosphorus and sulfur atoms, these organic compounds and their complexes might demonstrate unique specific physicochemical properties. Therefore in this paper we report on functionalized dimethyl(phenylsulfonyl)amidophosphate [$PhSO_2NHP(O)(OMe)_2$] compounds obtained by the attachment of substituents with the aromatic function to the phosphorus atom: dibenzyl(phenylsulfonyl)amidophosphate (H**L1**) and bis(4-methylphenyl)(phenylsulfonyl)amidophosphate (H**L2**) (Scheme 1, at the bottom). Tetramethyl[biphenyl-4,4′-diyldi(sulfonyl)]bis(amidophosphate) (H**L3**) is a dimer analog of $PhSO_2NHP(O)(OMe)_2$ which bears two chelate functions and which is expected to bind two lanthanide ions. To explore the acid nature of the NH group of the synthesized compounds, sodium salts Na**L1**, Na**L2** and Na_2**L3** were prepared and studied.

2. Experimental

2.1. Materials and methods

All reagents were purchased from commercial sources and used without further purification. Solvents were dried and purified by

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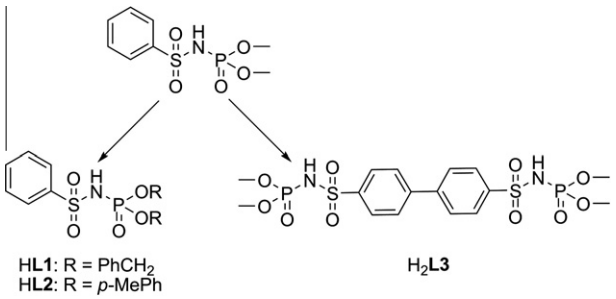


Scheme 1. Synthesized compounds H**L1**, H**L2** and H_2**L3**.

standard methods. NMR spectra were recorded on Varian Mercury 400 NMR spectrometer at 25 °C. ^{1}H and ^{31}P spectra were recorded at 400 and 162.1 MHz, respectively. Chemical shifts are reported with reference to $SiMe_4$ (^{1}H) and H_3PO_4 (^{31}P). IR samples were prepared as KBr pellets and spectra were recorded with a Perkin–Elmer Spectrum BX spectrometer in the range of 4000–400 cm^{-1}. Elemental analysis (C, H, N, S) were performed using EL III Universal CHNOS Elemental Analyzer.

2.2. Synthesis of H*L1*, H*L2*, H_2*L3* and their sodium salts

H**L1**, H**L2**, H_2**L3** were synthesized according to the Scheme 2.

2.2.1. Synthesis of H*L1*

The synthesis of H**L1** consists of three steps. The reaction between equimolar amounts of benzenesulfonamide $C_6H_5SO_2NH_2$ (1.57 g, 0.01 mol) and PCl_5 (2.08 g, 0.01 mol) was carried out according to the previously described method [26]. Then (phenylsulfonyl)phosphoramidic dichloride ($C_6H_5SO_2NPOCl_2$) was obtained by formolysis of (phenylsulfonyl)phosphorimidic trichloride ($C_6H_5SO_2NPCl_3$) according to the reported procedure [27]. Finally, H**L1** was synthesized according to the Scheme 2. The sodium metal (0.7 g, 0.03 mol) was added to the triple excess of phenylmethanol (9.73 g, 0.09 mol), and upon heating benzene (50 ml) was added to the obtained suspension. The mixture was cooled down and the (phenylsulfonyl)phosphoramidic dichloride (2.74 g, 0.01 mol) was added by small portions upon stirring. The resulting mixture was boiled during 1.5 h and the formed precipitate of NaCl was filtered off with suction and the filtrate was evaporated under vacuum. The oily precipitate was dissolved in the isopropanol (5 ml) and 50 ml of H_2O was added. The pH of the solution was adjusted to 2 by the addition of HCl_{conc} and the obtained thick oil quickly solidified. It was separated and recrystallized from the isopropanol as white fine-crystalline powder (yield 65%). $C_{20}H_{20}NO_5PS$ (H**L1**) (417.42): C 57.23 (calc 57.55); H 4.49 (4.83); N 3.23 (3.36); S 7.49 (7.68)%. IR (KBr): ν(NH) 2950 m, $\nu_{as}(SO_2)$ 1335 vs, ν(PO) 1245 s, $\nu_s(SO_2)$ 1175 s cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 4.93 (ddd, $^3J_{P,H}$ = 8 Hz, 4H, CH_2), 7.31 (m, 10H, C_6H_5), 7.52 (dd, 2H$_\beta$, C_6H_5), 7.61 (t, 1H$_\gamma$, C_6H_5), 7.89 (m, 2H$_\alpha$, C_6H_5). ^{31}P NMR (162.1 MHz, DMSO-d_6, 25 °C): δ = −4.33 (p, $^3J_{P,H}$ = 8 Hz).

Table 1
Crystallographic data for H**L2**, H_2**L3** and Na**L2**.

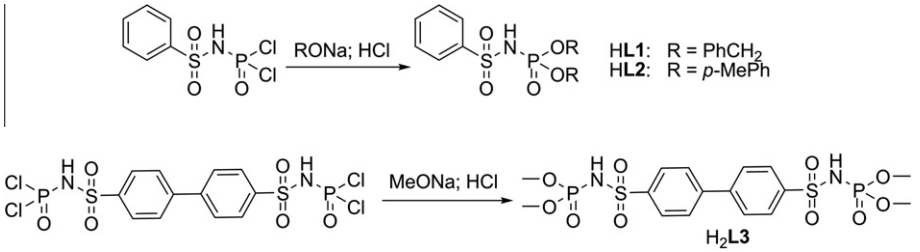
Compound	H**L2**	H_2**L3**	Na**L2**
Empirical formula	$C_{20}H_{20}NO_5PS$	$C_{16}H_{22}N_2O_{10}P_2S_2$	$C_{20}H_{19}NNaO_5PS$
Formula weight (g·mol^{-1})	417.40	528.42	439.38
Temperature (K)	293(2)	293(2)	293(2)
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P-1*	*P-1*	*P 21/c*
a (Å)	9.650(1)	6.733(1)	12.090(2)
b (Å)	10.381(1)	7.982(1)	5.8660(9)
c (Å)	10.898(1)	10.784(2)	30.648(4)
α (°)	70.19(1)	85.46(2)	90
β (°)	78.34(1)	77.41(1)	112.88(1)
γ (°)	82.190(9)	89.87(1)	90
V (Å^3)	1003.2(2)	563.7(2)	2002.5(6)
ρ_{calcd} (g·cm^{-3})	1.382	1.556	1.457
μ (mm^{-1})	0.272	0.434	0.296
F (000)	436	274	912
θ_{max} (°)	25.00	25.00	25.00
Reflections collected/ unique	5738/3400	2936/1795	12642/3479
Completeness to θ_{max} (%)	96.1	90.5	99.3
Data/restraints/ parameters	3400/0/255	1795/0/146	3479/0/264
Goodness-of-fit on F^2	1.09	1.03	0.60
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.035	*R*1 = 0.098	*R*1 = 0.042
	w*R*2 = 0.096	w*R*2 = 0.254	w*R*2 = 0.031
R indices (all data)	*R*1 = 0.047	*R*1 = 0.124	*R*1 = 0.180
	w*R*2 = 0.103	w*R*2 = 0.279	w*R*2 = 0.044

2.2.2. Synthesis of H*L2*

Compound H**L2** was prepared according to the reported procedure [28]. $C_{20}H_{20}NO_5PS$ (H**L2**) (417.42): C 57.32 (calc 57.55); H 4.68 (4.83); N 3.19 (3.36); S 7.52 (7.68)%. IR (KBr): ν(NH) 2975 s, $\nu_{as}(SO_2)$ 1345 vs, ν(PO) 1255 vs, $\nu_s(SO_2)$ 1180 s cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 2.31 (m, 6H, CH_3), 6.99 (d, 4H$_\alpha$, C_6H_4), 7.10 (d, 4H$_\beta$, C_6H_4), 7.49 (dd, 2H$_\beta$, C_6H_5), 7.60 (t, 1H$_\gamma$, C_6H_5), 7.84 (m, 2H$_\alpha$, C_6H_5). ^{31}P NMR (162.1 MHz, DMSO-d_6, 25 °C): δ = −13.6 (m).

2.2.3. Synthesis of H_2*L3*

The synthesis of H_2**L3** was carried out similarly to H**L2**. Ground biphenyl-4,4′-disulfonamide (p-$C_6H_4SO_2NH_2)_2$ (3.12 g, 0.01 mol) and PCl_5 (4.16 g, 0.02 mol) were refluxed in dioxane (10 ml) until no more of HCl was formed (checked with a gasometer) and then solvent was removed on a rotor vapor. Obtained [biphenyl-4,4′-diyldi(sulfonyl)]bis(phosphorimidic trichloride) (p-$C_6H_4SO_2NPCl_3)_2$ was formolysed and the precipitate of (p-$C_6H_4SO_2NHPOCl_2)_2$ was obtained. As the next step (Scheme 2), the methanol solution (20 ml) of sodium methanolate (2.16 g, 0.04 mol) was placed in a three-neck round-bottomed flask and cooled on an ice-bath. The



Scheme 2. Synthesis of H**L1**, H**L2** and H_2**L3**.