Chinese Chemical Letters Vol. 10, No. 11, pp.971-972, 1999

Synthesis, structure and spectroscopic properties of organophosphoryl polyoxotungstates of Formula α-$[R_2PW_9O_{34}]^{5-}$($R=C_6H_5P(S), C_6H_{11}P(O)$)

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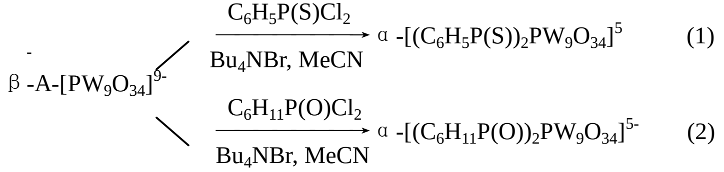
Abstract: Tetrabutylammonium salt of organophosphoryl derivatives of trivacant tungstophosphate of formula α-$[R_2PW_9O_{34}]^{5-}$ ($R=C_6H_5P(S)$, $C_6H_{11}P(O)$) have been prepared, purified and characterized by elemental analysis, IR, ^{31}P and ^{183}W NMR. According to spectroscopic observations and chemical analysis, the hybrid anion consists of an α-$[PW_9O_{34}]^{9-}$ framework on which are grafted two equivalent organophosphoryl groups through P-O-W bridges, and the IR spectral data show that these new species still retain the keggin structure.

Keywords: Polyoxometalates, organophosphorus, complex.

Interest and activity in the chemistry of polyoxometalates is largely driven by potential application in catalysis and medicine[1]. It has been recorgnized for a long time that the appropriate organic groups on the surface of polyoxometalates could modify the solubility and other physical properties of the complexes that would increase their utility and versatility in catalysis[2-4]. The reactivity of lacunary polyoxotungstates with organic and organometallic groups have been summarized[5]. To the best of our knowledge, the reaction of lacunary polyoxotungstates with organophosphonic acid was reported rarely, except for a unique study of Kim and Hill[6]on PhPO derivatives of monovacant tungsto-phosphate and -silicate, and Thouvenot[7] on RPO derivative of trivacant tungsto-phosphate. Here we report the synthesis and spectroscopic properties of the title compounds α-$[R_2PW_9O_{34}]^{5-}$ ($R=C_6H_5P(S)$, $C_6H_{11}P(O)$). Phenylthionophosphoro dichloride was prepared following literature[8]. Cyclohexanephosphonyl chloride was prepared according to published method[9]. The compounds β-A-$Na_8H[PW_9O_{34}]\cdot 24H_2O$[10] (0.8mmol) and Bu_4NBr (4.8mmol) were suspended in MeCN (20ml), $C_6H_5P(S)Cl_2$ or $C_6H_{11}P(O)Cl_2$ (1.6mmol) in 15ml of acetonitrile was added dropwise under vigorus stirring, and the mixture stirred overnight at reflux. The title compounds were obtained in 31～40% yields , and each compound has been characterized by elemental analysis, IR, ^{31}P and ^{183}W NMR. The overall reaction is

The formulation of tetrabutylammonium salts of $[(C_6H_5P(S))_2PW_9O_{34}]^{5-}$ and $[(C_6H_{11}P(O))_2PW_9O_{34}]^{5-}$ are in agreement with elemental analysis. The structural characterization of these new species is achieved through IR, ^{31}P and ^{183}W NMR investigation. The infrared spectra of two compounds are very similar. The P-C stretching vibration bands of organophosphoryl group are observed at 1130 cm^{-1} in **1** and at 1153cm^{-1} in **2**. The IR spectra of the compounds exhibit the four characteristic P-O_a, W-O_d, W-O_b-W and W-O_c-W asymmetric strectching vibrational peaks, indicating that these new complexes still retain the basic Keggin structure. The stretching vibrational bands [ν_{as}(W-O_d) and ν_{as}(W-O_b-W)] in the compounds shifted to the higher frequency, compared to the starting $[PW_9O_{34}]^{9-}$ anion. Obviously, the increase of ν_{as}(W-O_d) and ν_{as}(W-O_b-W) is due to the decrease of negative change on the polyoxoanions, weaking the anion cohesion. However, the P-O stretching vibration at 1080cm^{-1} in the spetrum of $PW_{12}O_{40}^{3-}$ is split into two bands at 1087 and 1028cm^{-1} in the spectra of the title compounds, which is indicative of the partial saturation of the complexes. The attachment of phosphoryl groups onto the polyoxotungstate surface is demonstrated by the resonances in the ^{31}P NMR spectra, which are all distinct from that of $C_6H_5P(S)Cl_2$ (δ =75.6ppm) or $C_6H_{11}P(O)Cl_2$ (δ =58.5ppm). For example, the ^{31}P NMR spectrum of **2** in CD_3CN presents two lines at 32.5ppm and -12.4ppm with a relative intensity of 2:1. The high-frequency resonance is attributed to the phosphoryl group, the low-frequency singlet is assigned to the central PO_4 unit of the polyoxotungstate. The relative intensity is consistent with the grafting of only two phosphoryl groups, and the single resonance at 32.5ppm indicates that the mode of attachment of the organophosphoryl groups to the lacunary anion is equivalent. In addition, the ^{183}W NMR spectrum of **2** in CD_3CN consists of five peaks of relative intensity 1:2:2:2:2, and chemical shifts are –38.9, -91.0, -135.7, -175.8 and –187.1 ppm, establishing that the compounds possess C_s symmetry in acetonitrile. This feature was observed for other RPO derivatives of tungstophosphate.All spectroscopic data show that P atom is connected to two tungsten atoms of the polyoxotungstate framework.



Acknowledgments

The support of the National Natural Science Foundation (No. 29571008) is gratefully acknowledged.

References

1. M. T. Pope , A. Muller, *Angew. Chem. Int. Ed. Engl.*, **1991,** *30*, 34.
2. N. Mizuno, M. Misono, *Chem. Rev.*, **1998,** *98*, 199.
3. M. Weeks, C. L. Hill, R. F. Schinazi, *J. Med. Chem.*, **1992,** *35*, 1216.
4. Q. H. Yang, H. C. Dai, J. F. Liu*, *Chem. Res. Chinese Unive.*, **1998,** *1*, 6.
5. P. Gouzerh , A. Proust, *Chem. Rev.*, **1998,** *98*, 77.
6. G. S. Kim, K. S. Hagen , C. L. Hill, *Inorg. Chem.*, **1992,** *31*, 5316.
7. C. R. Mayer, R. Thouvenot, *J. Chem. Soc., Dalton Trans.*, **1998,** 7.
8. B. Buchner, L. B. Lockchart, *Org. Synth.*, **1951,** *31*, 88.
9. J. O. Clayton, W. L. Jensen, *J. Am. Chem. Soc.*, **1948,** *70*, 3880.
10. R. Massart, R. Contant, J. M. Fruchart, J. P. Ciabrini , M. Fournier, *Inorg. Chem.*, **1977,** *16*, 2916.

Received 23 June 1999