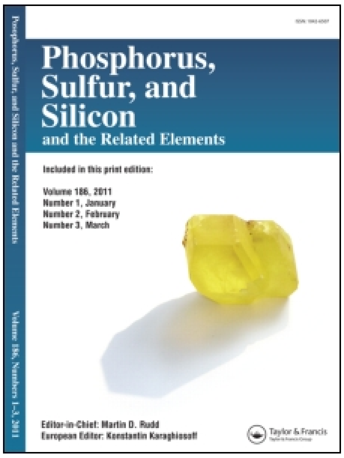

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AB INITIO CLUSTER CALCULATIONS OF THE CHEMICAL SHIFT TENSOR ON THE ^{31}P NUCLEI IN THE RING CRYSTAL PHOSPHATES

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AB INITIO CLUSTER CALCULATIONS OF THE CHEMICAL SHIFT TENSOR ON THE ^{31}P NUCLEI IN THE RING CRYSTAL PHOSPHATES

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The non-empirical quantum chemical calculations of the chemical shift tensor are used to predict the NMR spectrum form and to interpret the NMR spectrum obtained earlier. The calculated chemical shift tensors on the ^{31}P nuclei for some crystal phosphates are presented in the present work. All calculations are carried out by GIAO (Gauge-Invariant Atomic Orbital) method using cluster approach. As the clusters the isolated ring fragment of the corresponding crystal structures are chosen. Considering such approach, the agreement between calculations and experimental results is good.

Keywords: phosphates; *ab initio* calculations; chemical shift tensor

INTRODUCTION

The ^{31}P nuclei with zero quadrupole moment are excellent probes for NMR chemical shift studies of chemical bond features in the phosphate compounds. The correct quantum chemical calculation of chemical shift tensor and its comparison with the experimental data helps to control the weak changes of crystal structure and to predict the magnetic shielding character in the compounds which are not amenable to the NMR experiment. However, there are just a few such *ab initio* calculations [1].

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The method GIAO developed for the chemical shift tensor calculations in molecules [2] and implemented in the GAUSSIAN-94 program was firstly employed for the ring crystal phosphates in the present work.

DISCUSSION

The potassium trimetaphosphate $K_3P_3O_9$, potassium cyclo-hexaphosphate $K_6P_6O_{18}$ and sodium trimetaphosphate $Na_3P_3O_9$ were taken as the objects for calculations due to the available structural [3,4] and NMR experimental [5,6] data. We use the cluster approach for the quantum chemical calculations of these objects. It's natural to choose the isolated ring fragments of the structure $(P_3O_9)^{-3}$and $(P_6O_{18})^{-6}$ with the geometry of the corresponding crystals as the clusters for such *ab initio* calculations.

All calculations were carried out by MO LCAO SCF (Hartree-Fock-Roothaan) method with 6–311G* basis set of triple-zeta quality. To verify the chosen basis set the first calculations were carried out with the molecules PH_3, because the absolute value of the isotropic chemical shift for this compound is well-known [7] (598 p.p.m. and our calculated 597 p.p.m.).

The calculated parameters that determine unambiguously the shift tensor are shown in the TABLE I together with corresponding experimental MAS-NMR (Magic Angle sample Spinning Nuclear Magnetic Resonance) data. The average errors between theoretical and experimental data are 2%, 4% and 6% for isotropic values, anisotropy and asymmetry parameters respectively. These results show that our calculations are in a good agreement with experiments.

The chemical shift tensor is predicted also for potassium cyclo-hexaphosphate $K_6P_6O_{18}$ (there are no experimental data available nowadays).

The results in the TABLE I show that the contribution of K^+ cations into the calculated values is negligible.

RESULTS

In the present work it is shown that the cluster approach for the *ab initio* chemical shift tensor calculations with the triple-zeta quality basis set is successfully applied for the ring crystal phosphates.

TABLE I The calculated parameters of the shift tensor[a] and experimental MAS-NMR data for potassium and sodium ring crystal phosphates

Comp.	*Phosp. group*	*Isotropic chem. shift*[b]		*Anisotropy*		*Asymmetry parameter*	
		calc.	*expr.*	*calc.*	*expr.*	*calc.*	*expr.*
$K_3P_3O_9$	$(P_3O_9)^{-3}$	−18.0		−240.2		0.29	
		−18.3					
		−19.6					
	$(P_3O_9)^{-3}+3(K^+)$	−18.8	−18.2[5]	−243.0	−249.0[5]	0.28	0.31[5]
		−18.8	−19.9				
		−20.4	−21.2				
$K_6P_6O_{18}$	$(P_6O_{18})^{-6}$	−22.3	---	−205.0	---	0.40	---
		−22.5					
$Na_3P_3O_9$	$(P_3O_9)^{-3}$	−15.4	−15.5[6]	−237.3	−223.0[6]	0.42	0.48[6]
		−19.2	−18.6				
			−20.9				

a. The shift tensor parameters are determined with the following relations: isotropic chemical shift $\delta_i = (\delta_{11}+\delta_{22}+\delta_{33})/3$; anisotropy $\Delta\delta = \delta_{33} - (\delta_{11}+\delta_{22})/2$; asymmetry parameter $\eta = (\delta_{22} - \delta_{11}) / (\delta_{33} - \delta_i)$; where δ_{11}, δ_{22} and δ_{33} are the principal components of the shift tensor, providing $|\delta_{33} - \delta_i| \geq |\delta_{11} - \delta_i| \geq |\delta_{22} - \delta_i|$.

b. Shifts for different nonequivalent positions of ^{31}P atom are shown with respect to 85% H_3PO_4 in p.p.m.

The contribution of K^+ cations into the calculated shift tensor is negligible. In the 6-membered ring in the potassium metaphosphates by comparison with the 3-membered ring:

a) the value of the isotropic chemical shift is more negative (the magnetic shielding for ^{31}P atom is increased);

b) the absolute value of the shift tensor anisotropy is decreased.

The approach we have used and the high accuracy of the calculations make possible to predict the NMR parameters for $K_6P_6O_{18}$, which has no experimental data.

References

1. F.R. Prado, C. Giessner-Prettre, *J. Amer. Chem. Society*, **101**, 1737 (1979).
2. R. Ditchfield, *Mol. Phys.*, **27**, 789 (1974).
3. P.M. Bagieu-Beucher, *Acta cryst.*, **B32**, 1427 (1976).
4. H.M. Ondik, *Acta cryst*, **18**, 226 (1965).
5. A.-R. Grimmer and U. Haubenreisser, *Chem. Phys. Letters*, **99**, 487 (1983).
6. L. Griffiths, *J. Chem. Soc. Dalton Trans.*, 2247 (1986).
7. J. Mason, *Multinuclear NMR*, Plenum Press, (1987).