Solid-State ^{51}V NMR Study of Diperoxovanadium Complexes

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Introduction

Vanadium compounds have been widely used as orally administered drugs for diabetes mellitus treatments (*1*) since their coordination chemistry plays an important role in *in vitro* insulin-mimetic activity and *in vivo* antidiabetic blood glucose lowering activity. The general coordination number of vanadium in complexes with multi-dentate ligands ranges from four to seven and the coordination chemistry is directly associated with the functionality of the vanadium complexes (*2*). ^{51}V solid state NMR (SSNMR) uniquely provides valuable structural information i.e. the chemical shift anisotropy (CSA) and the electric field gradient (EFG), the two parameters that represent the local environment of the vanadium nucleus. Thus ^{51}V SSNMR spectroscopy is a powerful analytical tool to study vanadium compounds for understanding the relationships between the coordination geometry and functionality (ligand substitution). In this project, we utilize ^{51}V SSNMR spectroscopy to study four typical diperoxovanadium complexes $M_n[VO(O_2)_2L]\cdot mH_2O$ having remarkable inhibitory effects on the bovine heart tyrosine phosphatase as well as an insulin–mimetic bioactivity, where M = K^+, Na^+ or NH_4^+; L = oxalate, picolinate, bipyridine, and 1,10-phenanthroline; n = 3, 2, 1, 1, correspondingly; m = 1 – 5. The anions $[VO(O_2)_2L]^{n-}$ are abbreviated as bpVL (L = ox, pic, bipy, and phen). These four organic ligands represent three types of coordination atomic pairs (OO, ON and NN) and may have different steric hindrance effects. Coupled with standard variable temperature ^{13}C NMR experiments and density functional theory calculations, ^{51}V SSNMR provides a powerful probe of structure-activity relationships in the bpVL complexes.

Experimental

^{51}V SSNMR experiments were carried out on a Bruker DRX 600 NMR spectrometer using Bruker 2.5mm HX MAS probe at the NHMFL. The sample spinning rate ranged from 25 to 29 kHz. The ^{51}V chemical shift was referenced to neat $VOCl_3$.

Results and Discussion

Fig.1 shows the ^{51}V MAS NMR spectra of the four bpVL complexes. The shape of the sideband manifold consists of both the central transition sidebands and the satellite transition sidebands. The isotropic shifts (i.e. the centerbands) are -713, -748, -741, and -733 ppm for the bpVox, bpVpic, bpVbipy, and bpVphen, respectively, as indicated by the asterisks, which reflect the isotropic chemical shifts and the isotropic shift of the second-order quadrupolar interactions. The lineshapes of the centerbands, independent of the chemical shift anisotropies, strongly depend on the second-order quadrupolar interactions. The quadrupolar coupling constant C_Q, the asymmetric parameter η_Q, and the isotropic chemical shift δ_{iso} yielded from the lineshape simulations of the centerbands (the insets of Fig.1) are listed in Table 1.

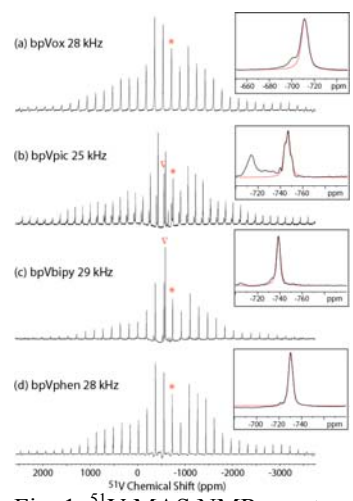

Fig. 1. ^{51}V MAS NMR spectra of four bpVL complexes (L=ox, pic, bipy, and phen).

Conclusion

The coordination agent in bioactive bpVL complexes has a significant effect on the ^{51}V EFG tensor and isotropic chemical shift. Combined with other data, we conclude that the coordination number of the vanadium center in bpVox changes from seven to six upon dissolution, while the coordination manners in bpVpic, bpVphen and bpVbipy remains unchanged in solid and solution states.

Table 1 ^{51}V SSNMR parameters for the four bpV complexes.

Complex	C_Q / MHz	η_Q	δ_{iso} /ppm	δ_{iso}*/ppm
bpVox	4.8 ± 0.5	0.90 ± 0.10	- 704 ± 5	-738
bpVpic	5.8 ± 0.5	0.35 ± 0.10	- 735 ± 5	-743
bpVbipy	4.0 ± 0.5	1.0 ± 0.1	- 732 ± 5	-746
bpVphen	4.0 ± 0.5	1.0 ± 0.1	- 725 ± 5	-742

Note: δ_{iso}*: ^{51}V chemical shifts obtained from their solution states in D_2O (with a concentration of 0.2 mol/L).

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References

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