Solvent Effects on the Isotropic NMR Shifts in Quinuclidine and Pyridine-Type Ligands Coordinated to the Paramagnetic Polyoxometalate, $[SiW_{11}Co^{II}O_{39}]^{6-}$

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The solvent effects on the isotropic NMR shifts in conformationally rigid ligands such as quinuclidine, pyridine, and 4-aminopyridine coordinated to the paramagnetic polyoxometalate, $[SiW_{11}Co^{II}O_{39}]^{6-}$ ($SiW_{11}Co$), are reported. For these complexes the ligand exchange is slow on the NMR time scale and pure ^1H NMR signals have been observed at room temperature. The signals for the $SiW_{11}Co$ complexes are shifted upfield when dimethyl sulfoxide-d_6 (DMSO) is added to a D_2O solution. The isotropic shifts are separated into contact and pseudocontact contributions by assuming that the contact shifts are proportional to the isotropic shifts of the same ligands coordinated to $[SiW_{11}Ni^{II}O_{39}]^{6-}$. It is shown that both the contact and pseudocontact shifts decrease (the absolute values of the pseudocontact shifts increase), when D_2O is replaced by DMSO. It is suggested that D_2O, a strong hydrogen bond donor, withdraws electron density from $[SiW_{11}Co^{II}O_{39}]^{6-}$, increasing the acidity of the cobalt ion toward the axial ligand. When D_2O is replaced by DMSO, the acidity of the cobalt ion in $SiW_{11}Co$ decreases, weakening the Co-N bond. Then both the contact and pseudocontact shifts are expected to decrease in agreement with the observed solvent effects.

Introduction

Several years ago we discovered that the exchange rates of some ligands coordinated to a cobalt(II) ion could be slowed by incorporating it in various polyoxometalates.[1,2] It has been shown that pyridine- and imidazole-type ligands coordinated to $[SiW_{11}CoO_{39}]^{6-}$ ($SiW_{11}Co$) or $[SiW_{11}NiO_{39}]^{6-}$ ($SiW_{11}Ni$) undergo slow exchange on the NMR time scale, exhibiting separate signals for the complexes and the free ligands in their ^1H and ^{13}C NMR spectra.[1,2] Well-resolved NMR spectra of ligands coordinated to paramagnetic polyoxometalates can provide useful information on both the ligands and polyoxometalates.[3,4]

While studying ^1H NMR spectra of piperidine derivatives coordinated to $SiW_{11}Co$ in D_2O and DMSO, we have observed that solvents cause remarkable effects on the isotropic shifts. Since piperidine derivatives are conformationally flexible, the solvent effects may be caused by conformational changes. So we have studied ^1H NMR spectra of conformationally rigid ligands such as quinuclidine, pyridine, and 4-aminopyridine coordinated to $SiW_{11}Co$ in D_2O and DMSO. Surprisingly, large solvent effects have still been observed for these systems.

^1H NMR spectra of quinuclidine coordinated to bis(2,4-pentanedionato)cobalt(II) and -nickel(II) were reported before.[5] But these systems exhibited averaged NMR signals for the free ligands and the complexes, for the ligand exchange was fast on the NMR time scale. ^1H NMR spectra of pyridine and 4-aminopyridine coordinated to $SiW_{11}Co$ and $SiW_{11}Ni$ in D_2O were reported before.[1,6]

Experimental

$K_6[SiW_{11}Co(H_2O)O_{39}]\cdot nH_2O$ and $K_6[SiW_{11}Ni(H_2O)O_{39}]\cdot nH_2O$ were prepared according to the methods of Simmons[7] and Weakley *et al.*[8] Quinuclidine, pyridine, and 4-aminopyridine were purchased from Aldrich.

NMR samples were prepared by dissolving a polyoxometalate and a ligand in a 1 : 1 molar ratio in D_2O, D_2O-DMSO, or DMSO. As the pH of the aqueous solution containing quinuclidine was *ca.* 11.8, the polyoxometalate decomposed slowly. Still good NMR spectra could be observed for a few hours after preparation of the sample. When the pH of the solution was lowered, no NMR spectrum for the complex was observed. The complexes were stable in DMSO. The $SiW_{11}Co$ complexes of pyridine derivatives were stable in D_2O and DMSO.

^1H NMR spectra were obtained with a Varian Gemini-300 or -200 spectrometer equipped with a 5-mm broadband probe. NMR measurements were made at ambient temperature (22-25 °C). The line-broadening factor used in exponential apodization was 20 Hz. Pulses of 90° (10 μs) were used, and the acquisition time was 0.2 s. No extra delay time was introduced between pulses. The residual water resonance in each spectrum was saturated by irradiating with a single frequency pulse which was gated off during acquisition. Sodium salt of 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid (TSP) and TMS were used as internal references.

Results and Discussion

Quinuclidine. ^1H NMR spectra of D_2O, D_2O-DMSO, and DMSO solutions containing quinuclidine (quin) and $SiW_{11}Co$ are shown in Figure 1. The ^1H NMR spectrum of quinuclidine in $CDCl_3$ was reported before (α-H, 2.9; β-H, 1.6; γ-H, 1.8 ppm).[5] The two strong peaks at 1-4 ppm are attributed to α-H and β-H of the free ligand. The weak signal of γ-H is hidden under that of β-H. Peaks from the complex are readily identified by their linewidths[9] and relative intensities. The broadest peak at the lowest field is assigned to α-H, the weakest peak at the highest field to γ-H, and the medium-field peak to β-H. The peaks at 4.7 ppm in D_2O and at 3.5 ppm in DMSO come from HDO or H_2O. On going from D_2O to DMSO the α-, β-, and γ-H peaks

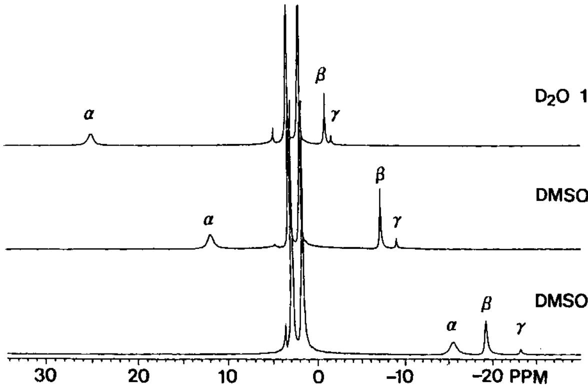

Figure 1. ^{1}H NMR spectra of (a) D_2O, (b) 2 : 1 (by volume) D_2O-DMSO, and (c) DMSO solutions containing quinuclidine and $SiW_{11}Co$ in a 1 : 1 molar ratio. The peaks originating from the complex are labeled.

are shifted upfield by 40, 18, and 21 ppm, respectively. The isotropic shifts change linearly as a function of the volume percent of D_2O in the mixed solvent (Figure 2).

The isotropic NMR shifts (δ_{iso}) in a paramagnetic system contain contact (δ_{con}) and pseudocontact shifts (δ_{dip}).

$$\delta_{iso} = \delta_{con} + \delta_{dip} \tag{1}$$

Contact shifts occur when unpaired electron density is transferred from the metal to the ligand nucleus in question, whereas pseudocontact shifts arise from a through-space dipolar interaction between the electronic and nuclear magnetic moments.[10]

The contact and pseudocontact contributions to the isotropic shifts may be separated in the following way. Octahedral nickel complexes have negligible magnetic anisotropy, and their isotropic shifts come mainly from the contact shifts.[11] Since both Co^{2+} and Ni^{2+} ions in octahedral environments have two electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals, and π electron cannot be delocalized onto quinuclidine, the contact shifts in the $SiW_{11}Co$ complex may be assumed to be proportional to the corresponding isotropic shifts for the $SiW_{11}Ni$ complex. ^{1}H NMR spectra of D_2O and DMSO solutions containing quinuclidine and $SiW_{11}Ni$ are shown in Figure 3. Considerable solvent-dependent shifts are also observed, although they are much smaller than those for the $SiW_{11}Co$ complex. Isotropic shifts for the protons in the quinuclidine are listed in Table 1.

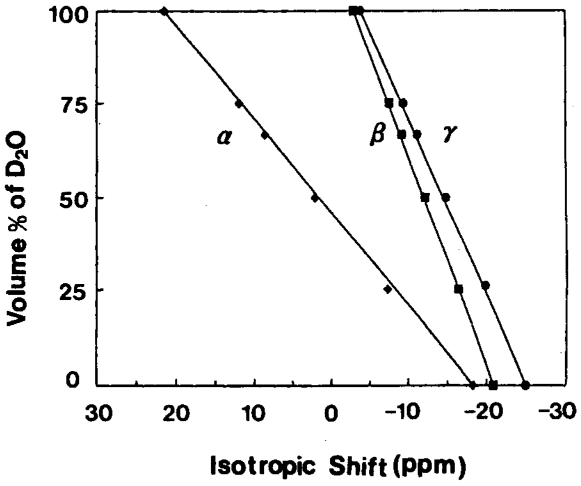

Figure 2. Isotropic shifts of protons in quinuclidine coordinated to $SiW_{11}Co$ as a function of the volume percent of D_2O in the D_2O-DMSO mixed solvent.

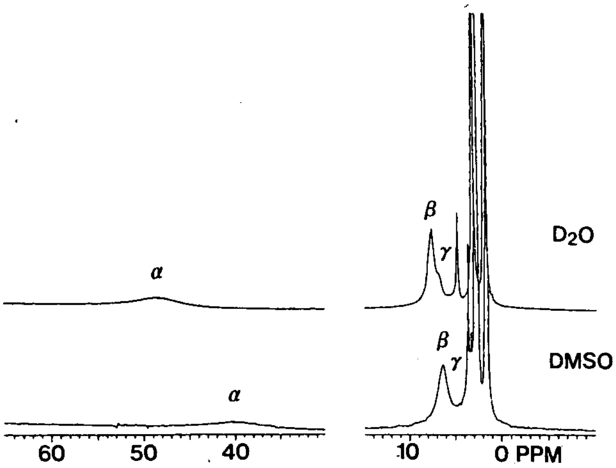

Figure 3. ^{1}H NMR spectra of (a) D_2O and (b) DMSO solutions containing quinuclidine and $SiW_{11}Ni$ in a 1 : 1 molar ratio. The peaks originating from the complex are labeled.

The pseudocontact shift may be expressed as[10]

$$\delta_{dip} = \frac{\mu_o}{4\pi r^3} \times [\{\chi_{zz} - (\chi_{xx} + \chi_{yy})/2\} \times (3\cos^2\theta - 1) + (\chi_{xx} - \chi_{yy}) \times \sin\theta \cos 2\phi] \tag{2}$$

where χ_{xx} etc. are magnetic susceptibility components, and other symbols have their usual meaning. The $SiW_{11}Co$(quin) complex exhibits only three NMR signals originating from α-, β-, and γ-H. This means that the ligand is rotating rapidly about the Co-N axis and/or there is no in-plane magnetic anisotropy; otherwise, more than three peaks would be observed. When the in-plane anisotropy term in Eq. (2) is neglected, the pseudocontact shift is given by

$$\delta_{dip} = \frac{\mu_o \{\chi_{zz} - (\chi_{xx} + \chi_{yy})/2\}}{4\pi} \times \frac{(3\cos^2\theta - 1)}{r^3} \tag{3}$$

So the isotropic shifts in the $SiW_{11}Co$ complex may be expressed as

$$\delta_{iso}(Co) = C_1 \times \delta_{iso}(Ni) + C_2 \times \frac{(3\cos^2\theta - 1)}{r^3} \tag{4}$$

where C_1 and C_2 are proportionality constants. Using the δ_{iso}

Table 1. Geometric factors (in Å^{-3}) and isotropic shifts (in ppm) for quinuclidine

	Geometric factor*	D_2O solutions		DMSO solutions	
		$SiW_{11}Ni$	$SiW_{11}Co$	$SiW_{11}Ni$	$SiW_{11}Co$
α-H	0.02144	45.7	21.5	35.0	−18.3
β-H	0.01113	6.0	−3.0	4.8	−20.9
γ-H	0.01004	4.9	−3.9	−	−25.0

*Taken from ref 5.

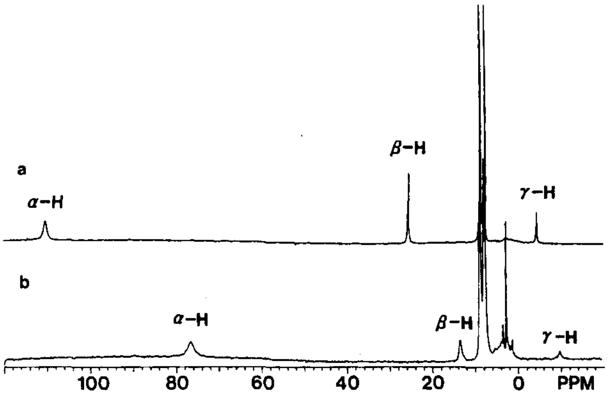

Figure 4. ^{1}H NMR spectra of (a) D_2O and (b) DMSO solutions containing pyridine and $SiW_{11}Co$ in a 1 : 1 molar ratio.

values for the α-H and β-H,[12] and geometric factors given in Table 1, we get C_1=0.799 and C_2= – 700 ppm $Å^3$ for the D_2O solution. A calculated value of δ_{iso} for γ-H, – 3.1 ppm, is in reasonable agreement with the observed value, – 3.9 ppm. A similar calculation for the DMSO solution produces C_1=0.850 and C_2= – 2246 ppm $Å^3$. Values of C_1 for the two solvents are similar, indicating that the contact shifts in the $SiW_{11}Co$ complex is about 80% of those in the $SiW_{11}Ni$ complex in both solvents. However, the C_2 value for the DMSO solution is about three times as large as that for the D_2O solution. According to Eq. (3), this means that the magnetic anisotropy in the $SiW_{11}Co$(quin) complex increases three-fold when D_2O is replaced by DMSO.

When the solvent effect on the isotropic shift is separated into contact and pseudocontact contributions for α-H (see below), it is seen that the pseudocontact contribution is dominant.

	δ_{con}	δ_{dip}	δ_{iso}
D_2O	36.5	– 15.0	21.5
DMSO	29.8	– 48.1	– 18.3
Shift	– 6.7	– 33.1	– 39.8

Pyridine. Similar experiments have been carried out for pyridine coordinated to $SiW_{11}Co$. ^{1}H NMR peaks are shifted upfield when D_2O is replaced by DMSO; see Figures 4 and 5. The isotropic shift data for $SiW_{11}Co$ and $SiW_{11}Ni$ complexes are summarized in Table 2.

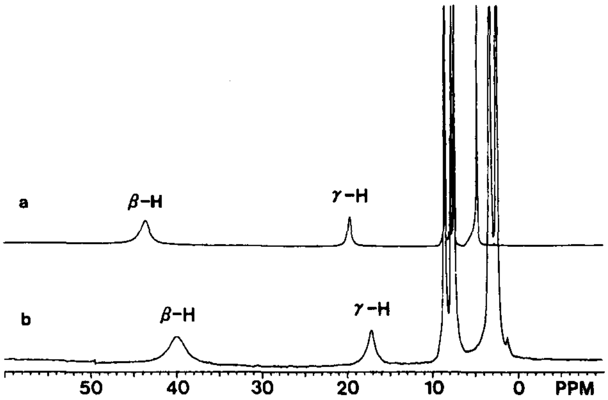

Figure 5. ^{1}H NMR spectra of (a) D_2O and (b) DMSO solutions containing pyridine and $SiW_{11}Ni$ in a 1 : 1 molar ratio.

Table 2. Geometric factors (in $Å^{-3}$) and isotropic shifts (in ppm) for pyridine

	Geometric factor[a]	D_2O solutions		DMSO solutions	
		$SiW_{11}Ni$	$SiW_{11}Co$	$SiW_{11}Ni$	$SiW_{11}Co$
α-H	0.0233	133.9[b]	101.6	122.4[c]	67.9
β-H	0.0106	36.1	17.7	32.7	5.9
γ-H	0.0092	11.8	– 12.7	9.5	– 17.7

[a] Taken from ref 13. [b] Estimated from the δ_{iso} value of α-H in pyridine coordinated to $[Ni_3(PW_9O_{34})_2]^{12-}$. [c] Eastimated. See the text.

Separation of contact and pseudocontact contributions to the isotropic shifts of the $SiW_{11}Co$ complex of pyridine was discussed elsewhere.[6] The procedure is explained briefly here. Isotropic values of α- and β-H in pyridine are used to calculate the parameters C_1 and C_2 in Eq. (4), for the contribution of π electron delocalization to the isotropic shifts is negligible for these protons. Unfortunately the signals from α-protons in pyridine coordinated to $SiW_{11}Ni$ are too broad to be observed. The isotropic shift of α-H for the $SiW_{11}Ni$ complex in D_2O is estimated from the value for pyridine coordinated to $[Ni_3(PW_9O_{34})_2]^{12-}$. And the corresponding value in DMSO is estimated by assuming that the ratios of δ_{iso} values for α- and β-protons are the same in D_2O and DMSO.

Using the δ_{iso} values given in Table 2, we get C_1=1.149 and C_2= – 2244 ppm $Å^3$ for D_2O and C_1=1.087 and C_2= – 2798 ppm $Å^3$ for DMSO. Again the solvent effect on the isotropic shift is separated into contact and pseudocontact contributions for α-H below. Here the contact and pseudocontact contributions are comparable.

	δ_{con}	δ_{dip}	δ_{iso}
D_2O	153.9	– 52.3	101.6
DMSO	133.1	– 65.2	67.9
Shift	– 20.8	– 12.9	– 33.7

4-Aminopyridine. ^{1}H NMR spectra of 4-aminopyridine coordinated to $SiW_{11}Co$ and $SiW_{11}Ni$ in D_2O and DMSO are similar to those of pyridine shown above. The isotropic shift data for $SiW_{11}Co$ and $SiW_{11}Ni$ complexes are summarized in Table 3.

Contact and pseudocontact contributions to the isotropic shifts were separated by the method described above for the pyridine complex. Using the δ_{iso} values given in Table 3, we get C_1=1.072 and C_2= – 729 ppm $Å^3$ for D_2O and C_1= 0.830 and C_1= – 1073 ppm $Å^3$ for DMSO. Again the solvent effect on the isotropic shift is separated into contact

Table 3. Geometric factors (in $Å^{-3}$) and isotropic shifts (in ppm) for 4-aminopyridine

	Geometric factor[a]	D_2O solutions		DMSO solutions	
		$SiW_{11}Ni$	$SiW_{11}Co$	$SiW_{11}Ni$	$SiW_{11}Co$
α-H	0.0233	130.3[b]	122.7	126.7[c]	80.2
β-H	0.0106	32.3	26.9	31.4	14.7

[a] Taken from ref 13. [b] Estimated from the δ_{iso} value of α-H in pyridine coordinated to $[Ni_3(PW_9O_{34})_2]^{12-}$. [c] Eastimated. See the text.

and pseudocontact contributions for α-H below. Here the contact contribution is dominant.

	δ_{con}	δ_{dip}	δ_{iso}
D_2O	139.7	−17.0	122.7
DMSO	105.2	−25.0	80.2
Shift	−34.5	−8.0	−42.5

Solvent Effects. Large solvent effects have been observed in the ^1H NMR spectra of quinuclidine, pyridine, and 4-aminopyridine coordinated to $SiW_{11}Co$. The α-H peaks are shifted upfield by 34-43 ppm when D_2O is replaced by DMSO. The shifts are as large as that caused by a large difference in the axial ligand basicity. For example, the chemical-shift difference of 4-aminopyridine (pK_a, 9.11) and 4-cyanopyridine (pK_a, 1.90) coordinated to $SiW_{11}Co$ in D_2O is 39 ppm.[6]

It was reported that the basicity of cyanide coordinated to low-spin ferric complexes was affected by solvents because of its proton accepting ability.[14] But no solvent effect was observed for pyridine and imidazole coordinated to the same complexes. The basicity of 4-aminopyridine toward $SiW_{11}Co$ may be affected by solvents because the amino group can form hydrogen bonds. But no such effect is expected for quinuclidine and pyridine. Therefore, solvent interactions operating through the coordinated ligands alone cannot explain the observed solvent effects. The solvent effects cannot be explained either by change in the geometry of the polyoxometalate, for the effects on the pseudocontact shifts depend strongly on the ligands.

We therefore suggest that the solvents cause effects on the interactions between $SiW_{11}Co$ and the ligands. When D_2O is replaced by DMSO, both the contact and pseudocontact shifts decrease (the absolute values of the pseudocontact shifts increase) for all three ligands. We have used splitting of d orbitals of Co(II) to explain the effect of the axial ligand basicity on the pseudocontact shifts in the $SiW_{11}Co$ complexes.[6] The orbital ground state configuration for the $SiW_{11}Co$ complexes of pyridine-type ligands places d_{xz}, d_{yz} below d_{xy} with a spacing Δ. A decrease in the axial ligand basicity will lower d_{xz}, d_{yz} relative to d_{xy} and hence increase Δ. An increase in Δ in turn will increase the magnitudes of the pseudocontact shifts (or decrease them for they have negative values).

$SiW_{11}Co$ has basic oxygen atoms on the surface, which form hydrogen bonds with D_2O. Such hydrogen bonds withdraw electron density from the heteropolyanion, increasing the Lewis acidity of the cobalt ion toward the axial ligand. Since no hydrogen bond can be formed between DMSO and $SiW_{11}Co$, the cobalt ion in $SiW_{11}Co$ is less acidic in DMSO than in D_2O. Therefore, the Co-N bond is weakened and elongated in DMSO,[15] decreasing the pseudocontact shifts, just as decrease of the axial ligand basicity does.[6] In addition, elongation of the Co-N bond is expected to decrease the contact shifts which arise from unpaired electron delocalization from the metal to the ligand nuclei. Decrease of both the contact and pseudocontact shifts in DMSO is in agreement with the observed solvent effects. In addition, the linear change in the isotropic shifts as a function of the concentration of DMSO in D_2O-DMSO mixed solvents (Figure 2) can be explained in terms of a gradual increase in the Co-N distance with increasing concentration of DMSO.

In summary, we have shown that solvents cause large effects on isotropic NMR shifts of various ligands coordinated to $SiW_{11}Co$. It is suggested that the solvent effects originate from change in the acidity of the cobalt ion toward the axial ligand by the solvent-heteropolyanion interactions. Although this explanation seems to be reasonable qualitatively, the magnitude of the solvent effect on the isotropic shifts is surprisingly large. Somehow the effect seems to be amplified. In addition, it is not clearly understood why the contributions of the contact and pseudocontact shifts to the solvent effects are quite different for different ligands.

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References

1. Ko, M.; Rhyu, G. I.; So, H. *Bull. Korean Chem. Soc.* **1993**, *14*, 500.
2. Ko, M.; Rhyu, G. I.; So, H. *Bull. Korean Chem. Soc.* **1994**, *15*, 673.
3. Woo, H. Y.; Kim, J. Y.; So, H. *Bull. Korean Chem. Soc.* **1995**, *16*, 1176.
4. Woo, H. Y.; So, H.; Pope, M. T. *J. Am. Chem. Soc.* **1996**, *118*, 621.
5. Yonezawa, T.; Morishima, I.; Ohmori, Y. *J. Am. Chem. Soc.* **1970**, *92*, 1267.
6. Kim, J. Y.; Park, S. M.; So, H. *Bull. Korean Chem Soc.* **1997**, *18*, 369.
7. Simmons, V. E. Ph.D. Thesis, Boston University (1963).
8. Weakley, T. J. R.; Malik, S. A. *J. Inorg. Nucl. Chem.* **1967**, *29*, 2935.
9. The linewidth is inversely proportional to the sixth power of the metal-nuclei distance. See Koenig, S. H. *J. Magn. Reson.* **1978**, *97*, 2113.
10. Happe, J. A.; Ward, R. L. *J. Chem. Phys.* **1963**, *39*, 1211.
11. Kluiber, R. W.; Horrocks, W. D., Jr. *J. Am. Chem. Soc.* **1965**, *87*, 5350.
12. The γ-H peak of the $SiW_{11}Ni$(quin) complex in DMSO has not been observed, indicating that its isotropic shift is small.
13. W. DeW. Horrocks, Jr. and D. DeW. Hall, *Inorg. Chem.* **1971**, *10*, 2368.
14. La Mar, G. N.; Gaudio, J. D.; Frye, J. S. *Biochim. Biophys. Acta* **1977**, *498*, 422.
15. If the Co-N distance depends on solvents, different geometric factors must be used for D_2O and DMSO solutions. However, a small change in Co-N distance does not change the semiquantitative results significantly.