

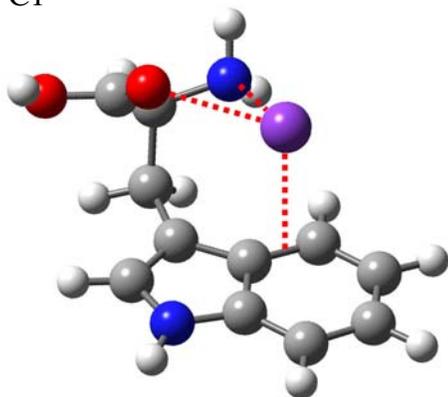
Supplementary Materials

IRMPD spectroscopy of metal-ion/tryptophan complexes

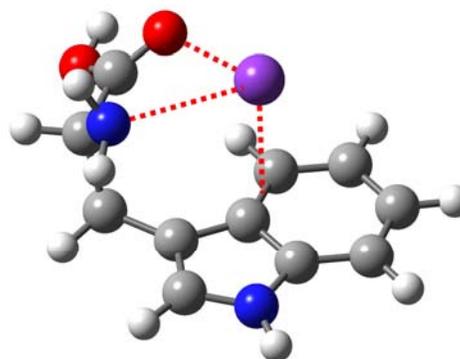
Nick C. Polfer,^{*†} Jos Oomens[†] and Robert C. Dunbar[#]

Isomer structures (K^+ complexes)

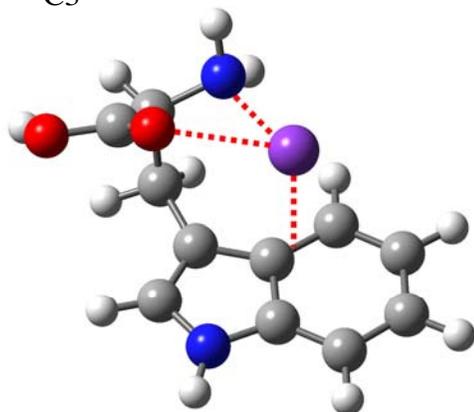
C1



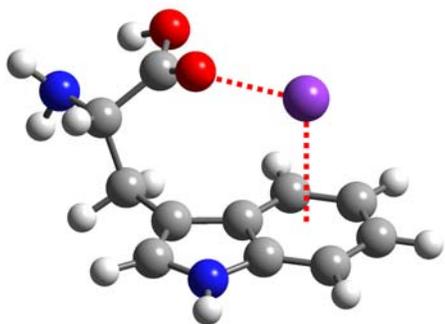
C2



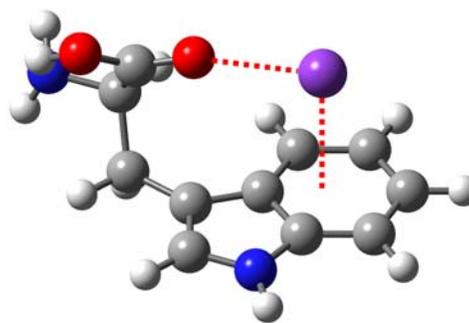
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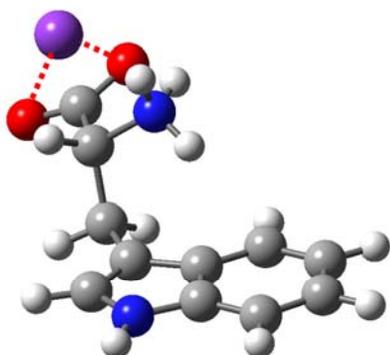
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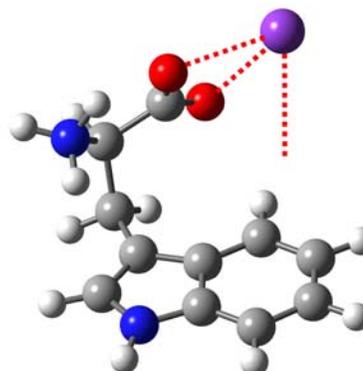
C5



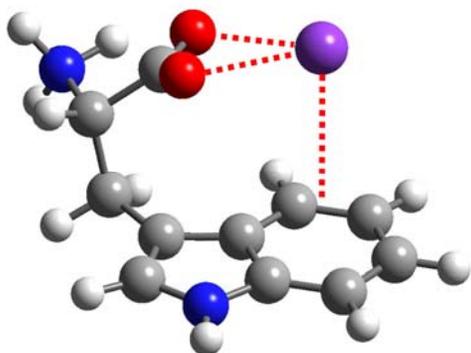
Z2



Z1



Z3



C6

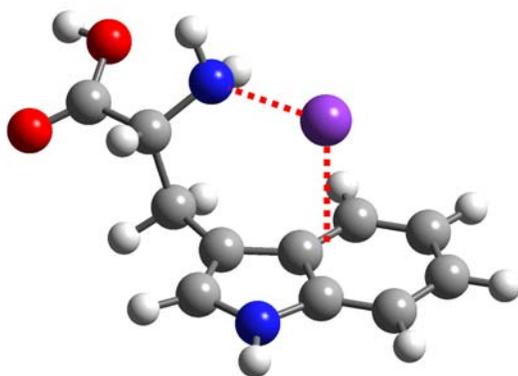


Fig. S1. The structural schemes for the nine isomeric forms for which calculations were made. The K^+ complexes are displayed here as illustrative of the ligand arrangements. Note that for ease of comparison the indole framework has been oriented identically in all cases. This has necessitated displaying the R- instead of the L-tryptophan form for several cases. Mirror reflection of the images between the L and R forms has of course no effect on the energetics or structural properties of these complexes.

Thermochemistry

Table S1. Energies of calculated isomers (kJ mol^{-1} relative to the most stable isomer for each metal ion.)

	N/O/Ring			O/Ring		Salt Bridge			N/Ring
	C1	C2	C3	C4	C5	Z2	Z1	Z3	C6
Li	0	9		16	18	31	37	48	
Na	0	8	24	9	13	22	25	38	
K	1	8	24	0	4	15	17	33	41
Rb	4	9		0	3	17	18		
Cs	6	12	28	0	3	18	19	a	38
Ag	0	6	27	20	27	47	40	42	19

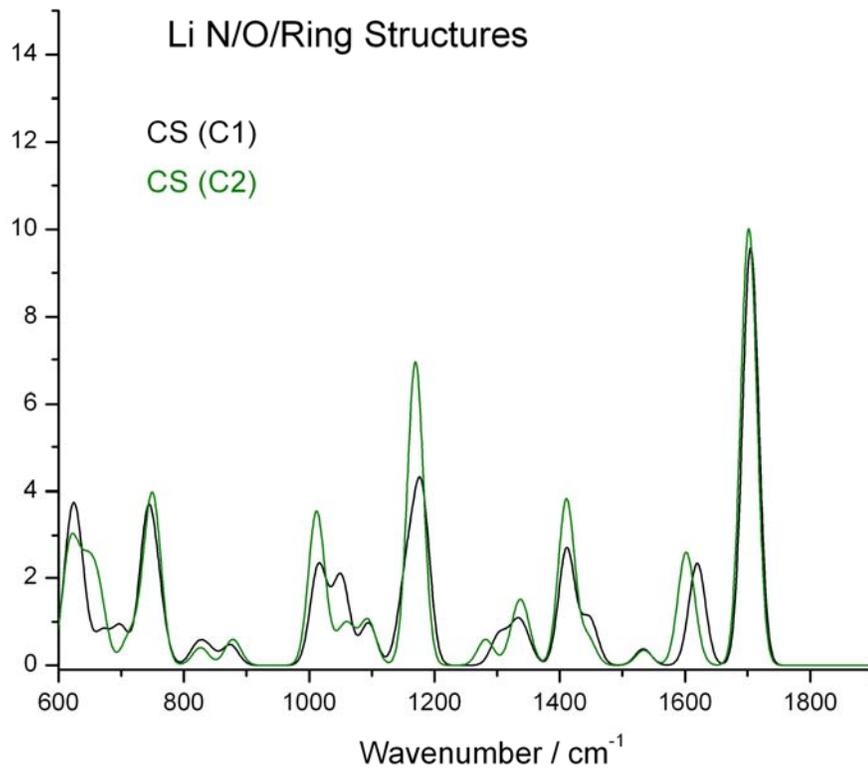
^a Rearranges spontaneously to O/Ring

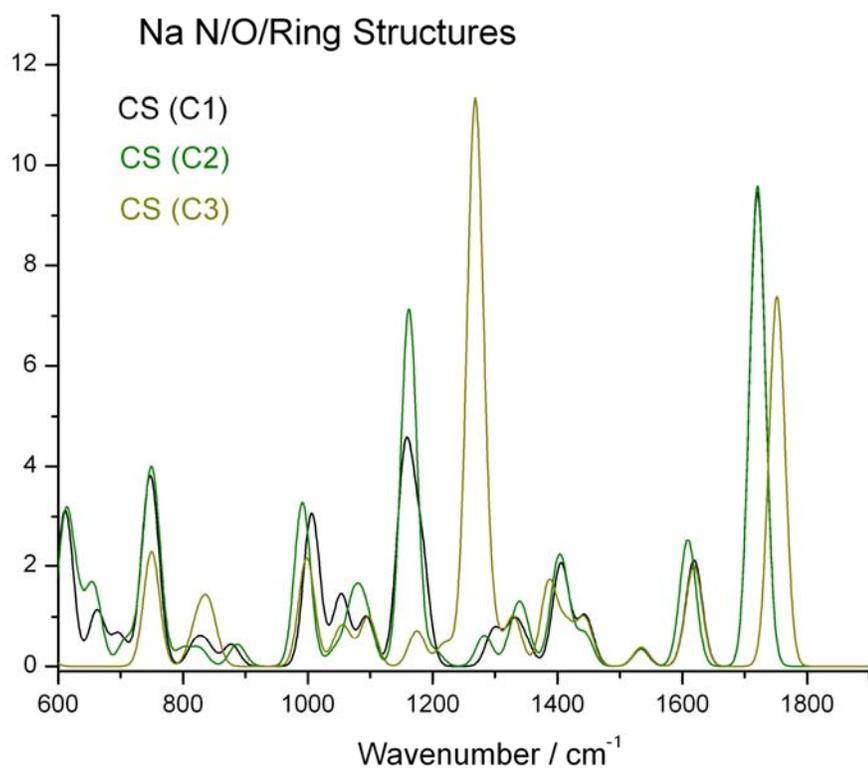
Table S2. Free energies of calculated isomers (kJ mol^{-1} relative to the most stable isomer for each metal ion.)

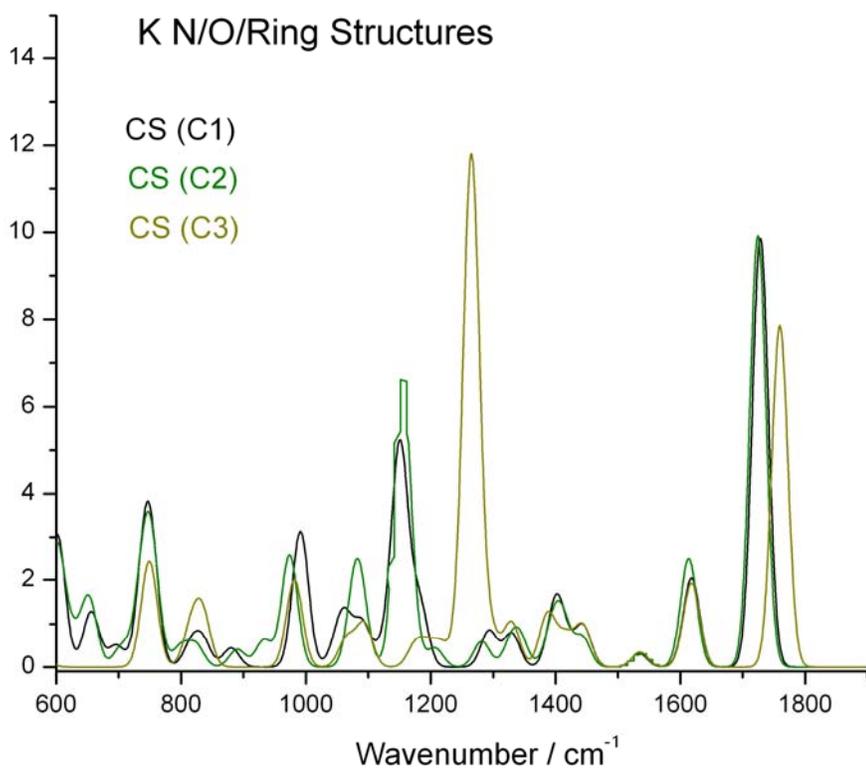
	N/O/Ring			O/Ring		Salt bridge			N/Ring
	C1	C2	C3	C4	C5	Z2	Z1	Z3	C6
Li	0	8		11	16	25	35	46	
Na	0	7	24	7	11	19	25	38	
K	2	7	24	0	4	13	16	33	34
Rb	4	9		0	3	17	18		
Cs	6	12	28	0	3	18	19		
Ag	0	5	27	19	24	41	40	41	

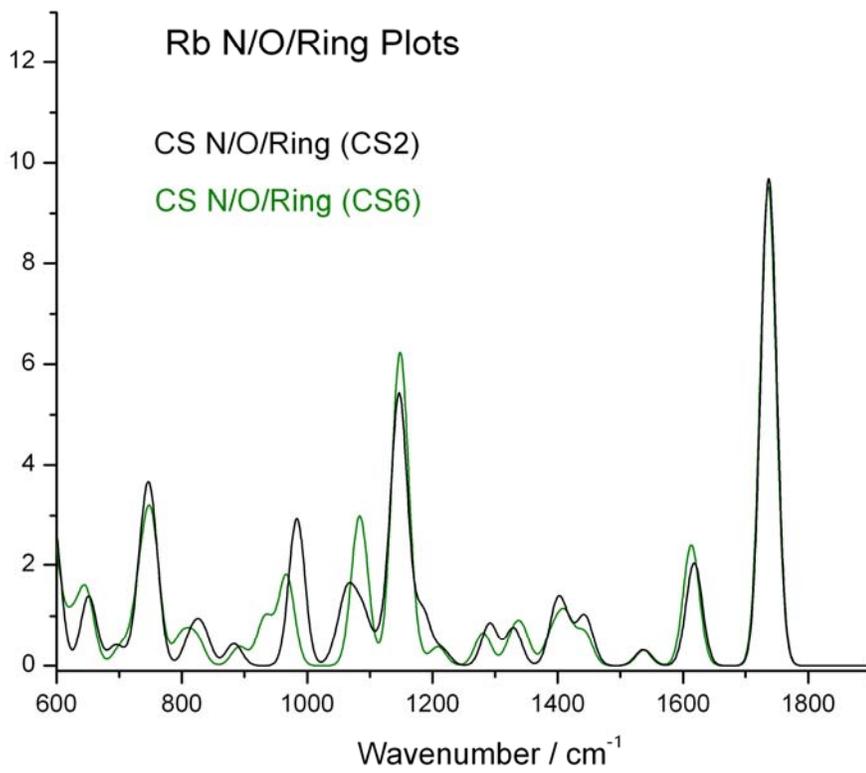
Calculated IR absorption spectra

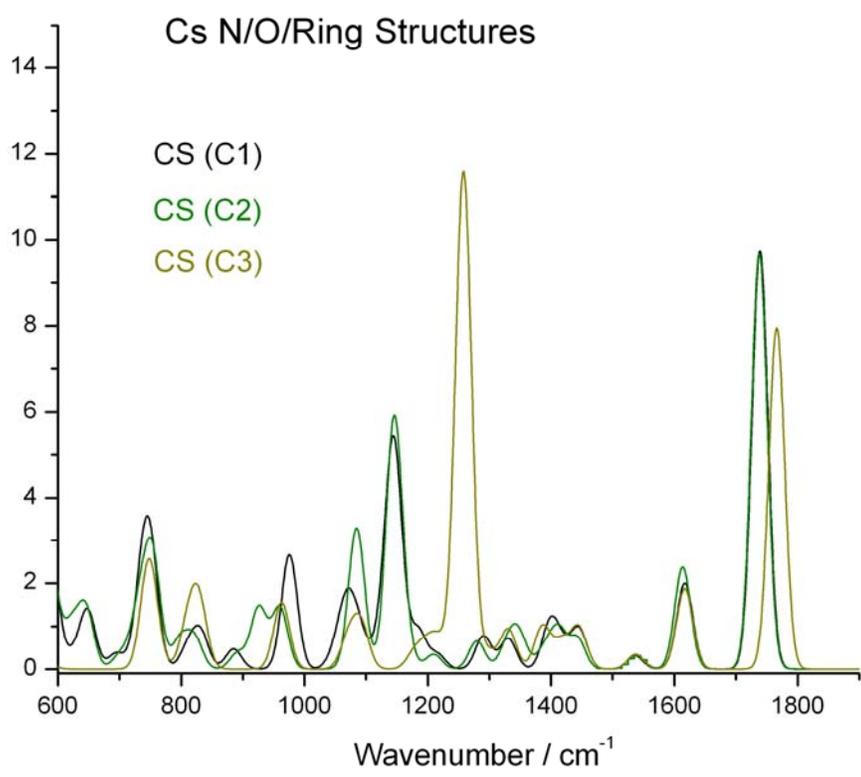
1. N/O/Ring structures

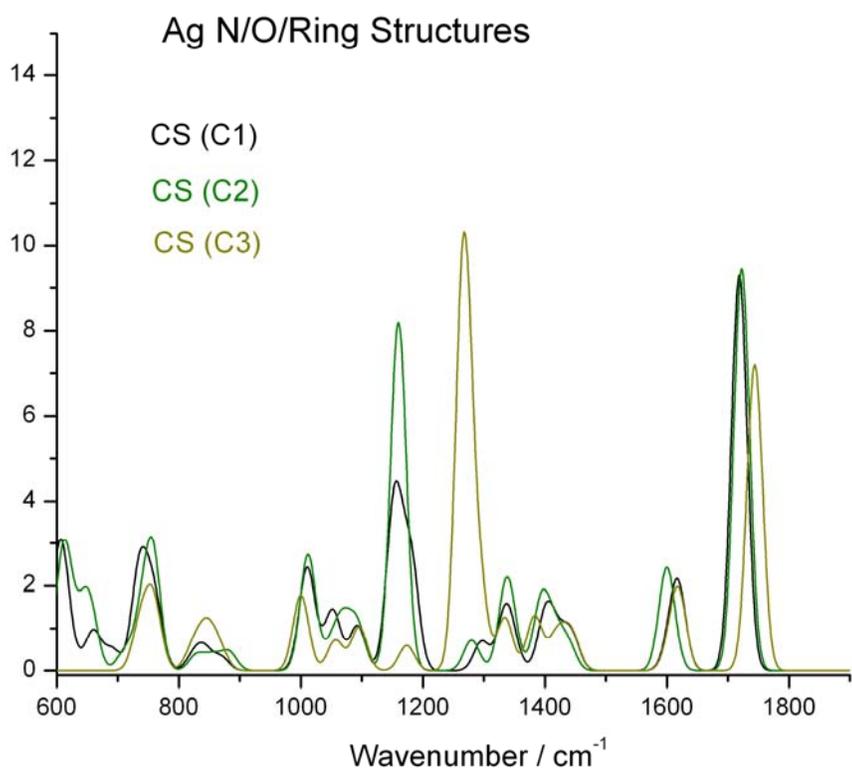




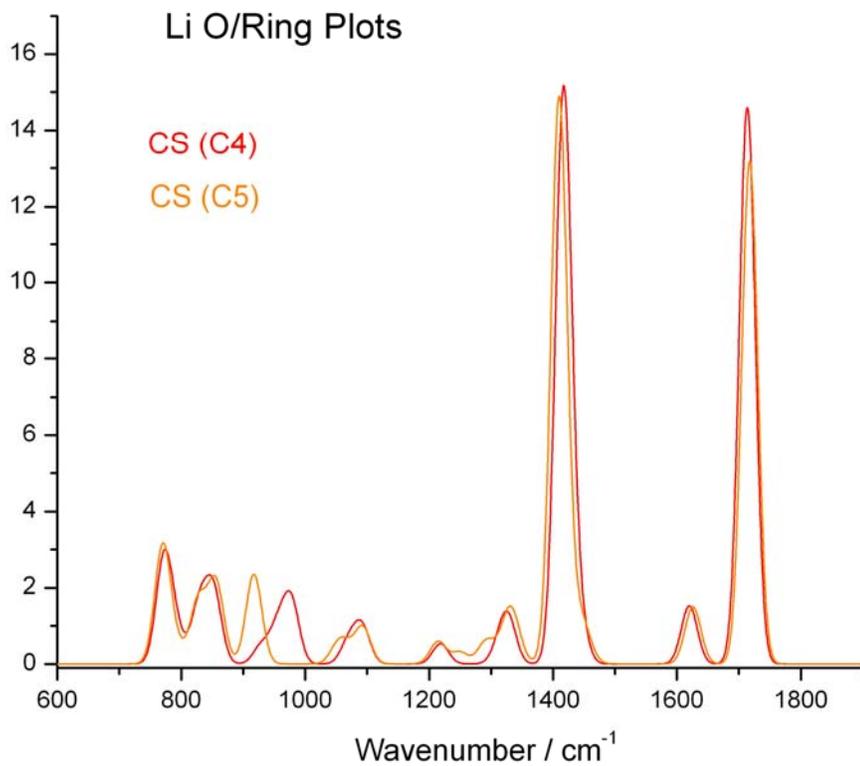


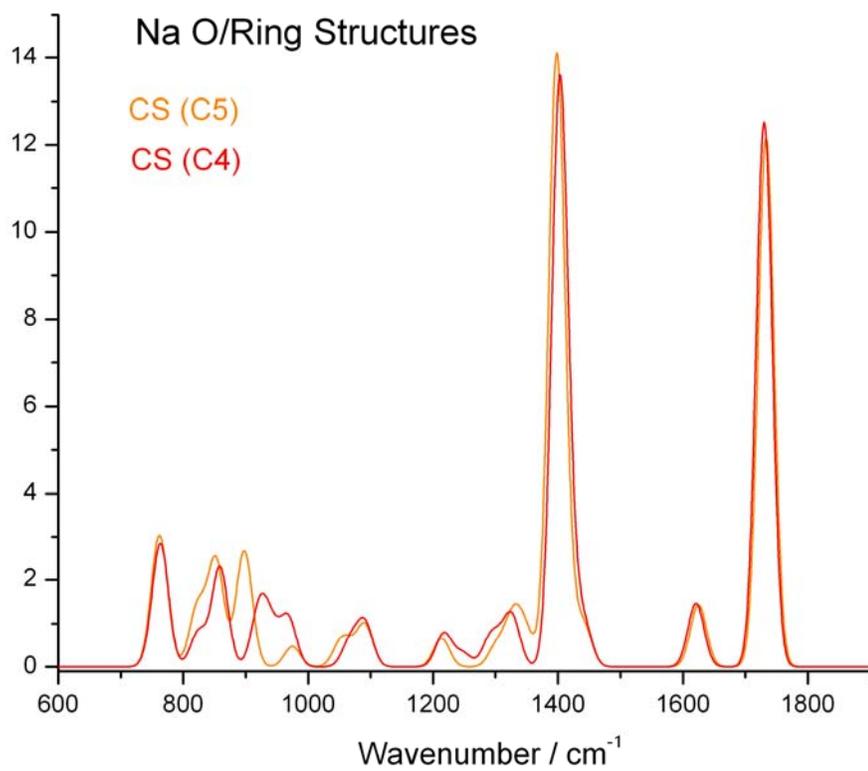


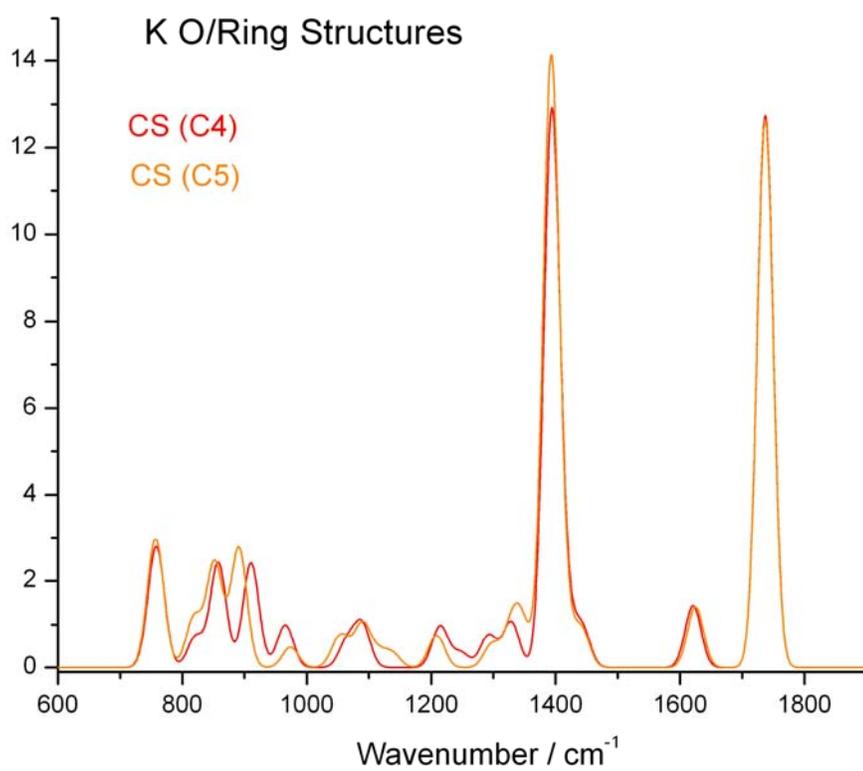


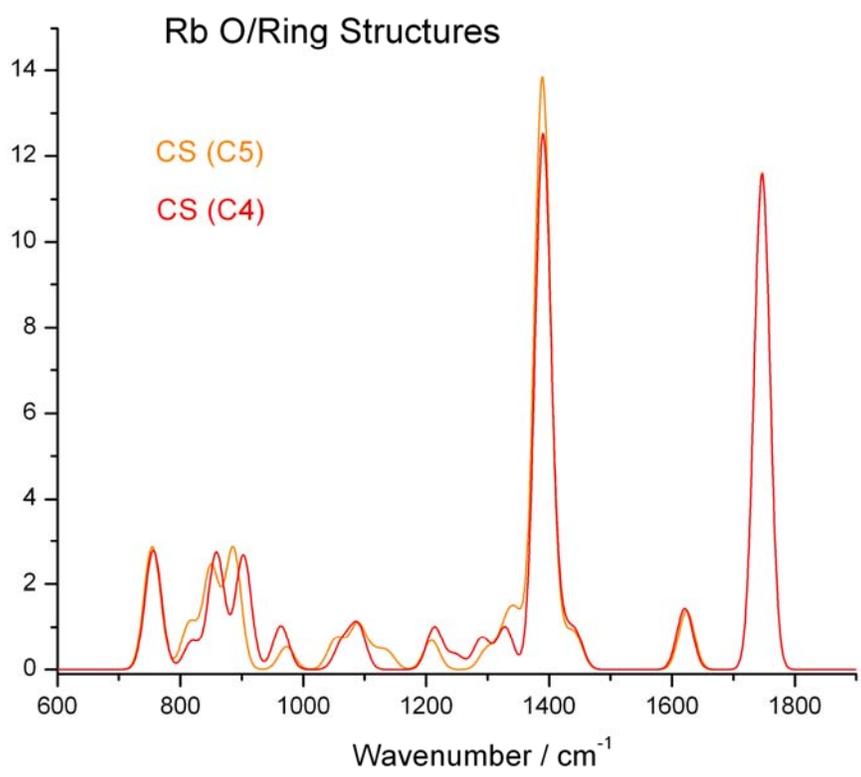


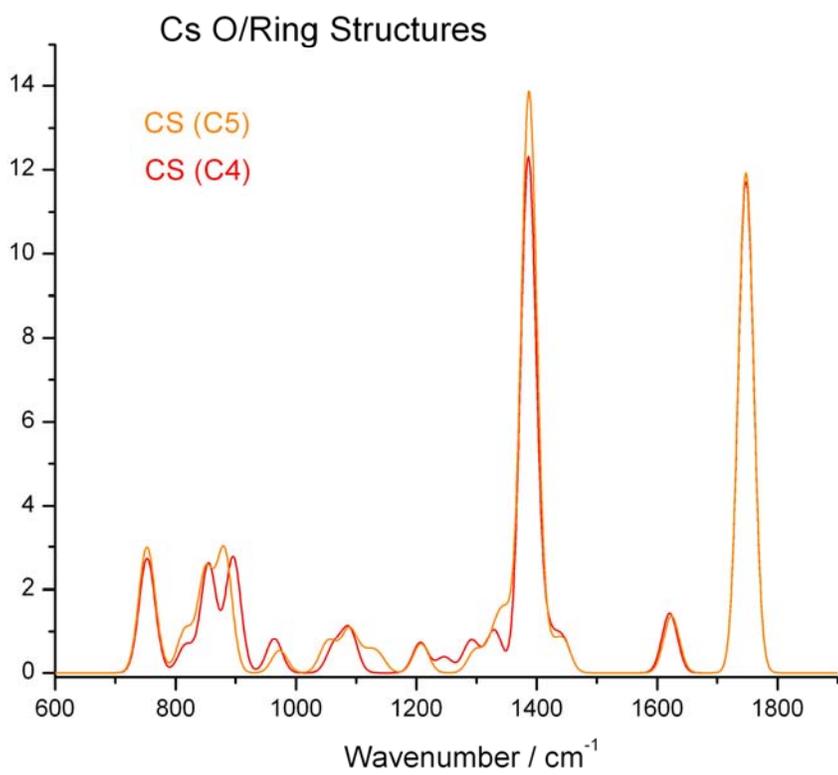
2. O/Ring structures

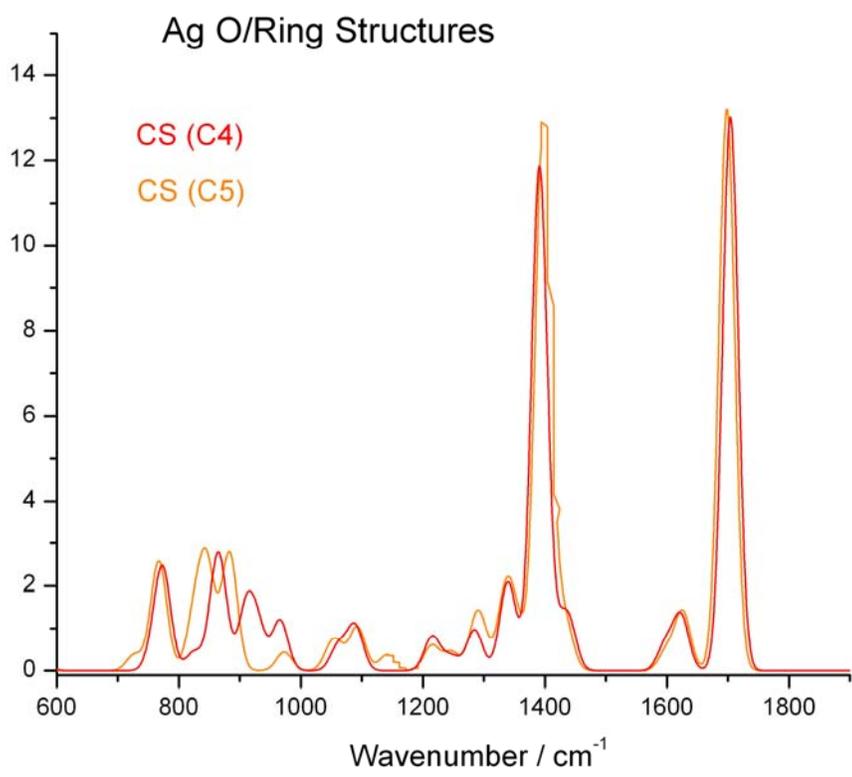




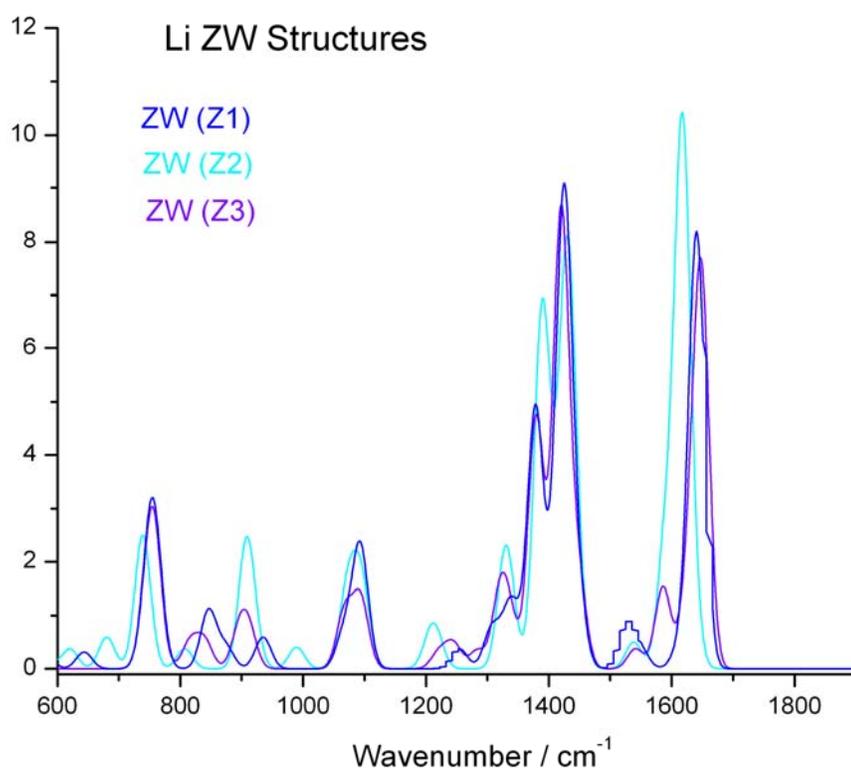


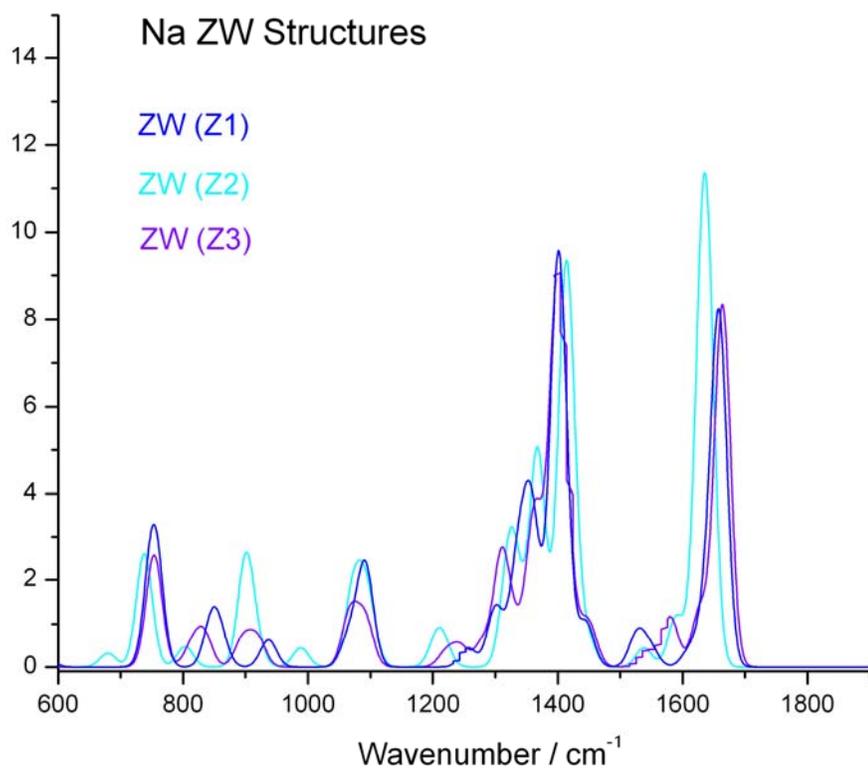


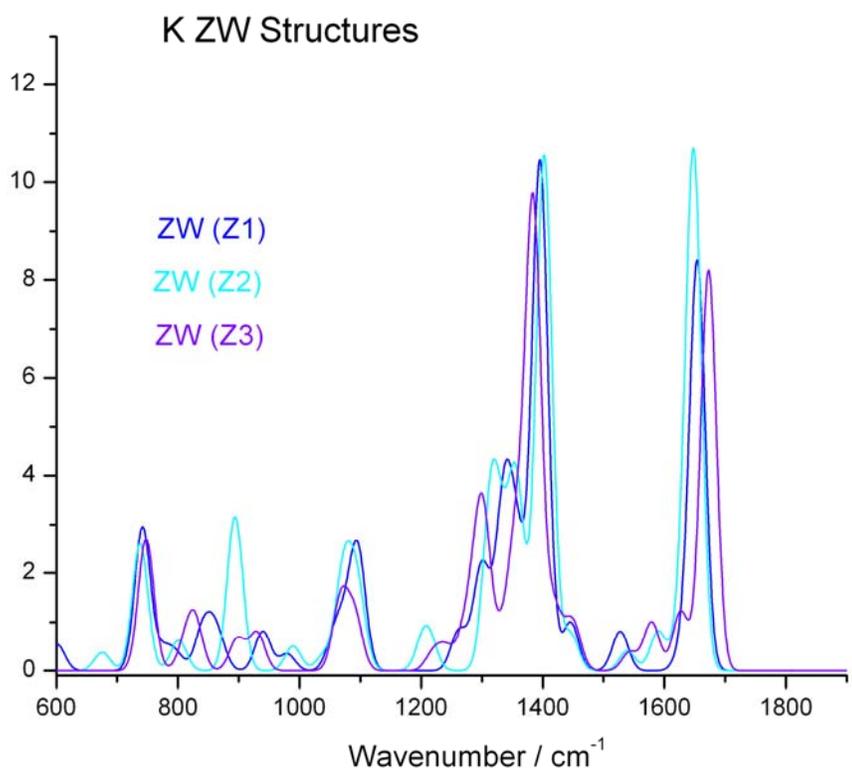


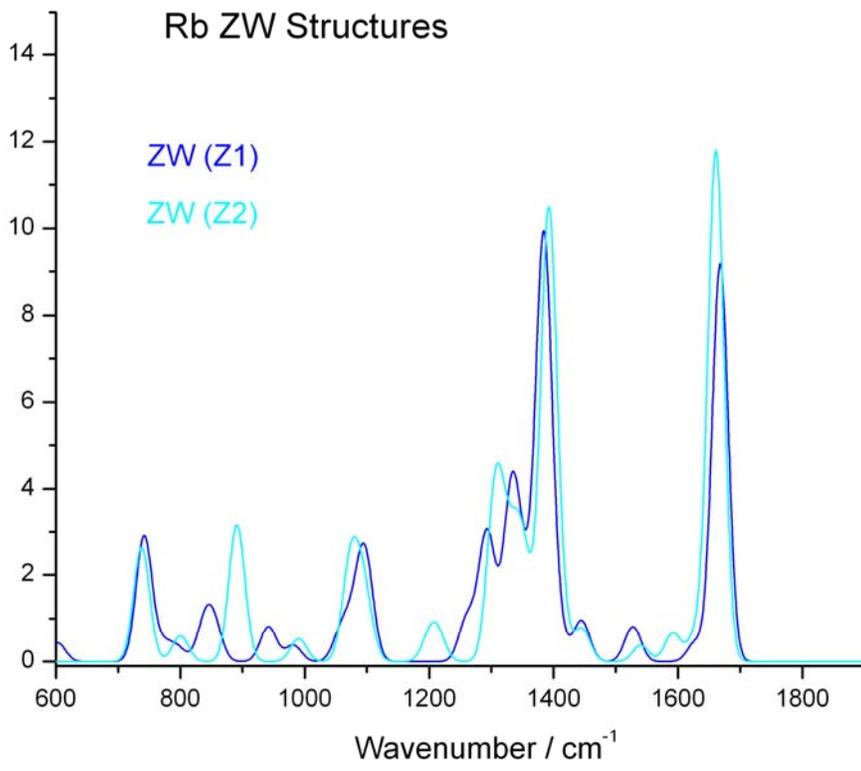


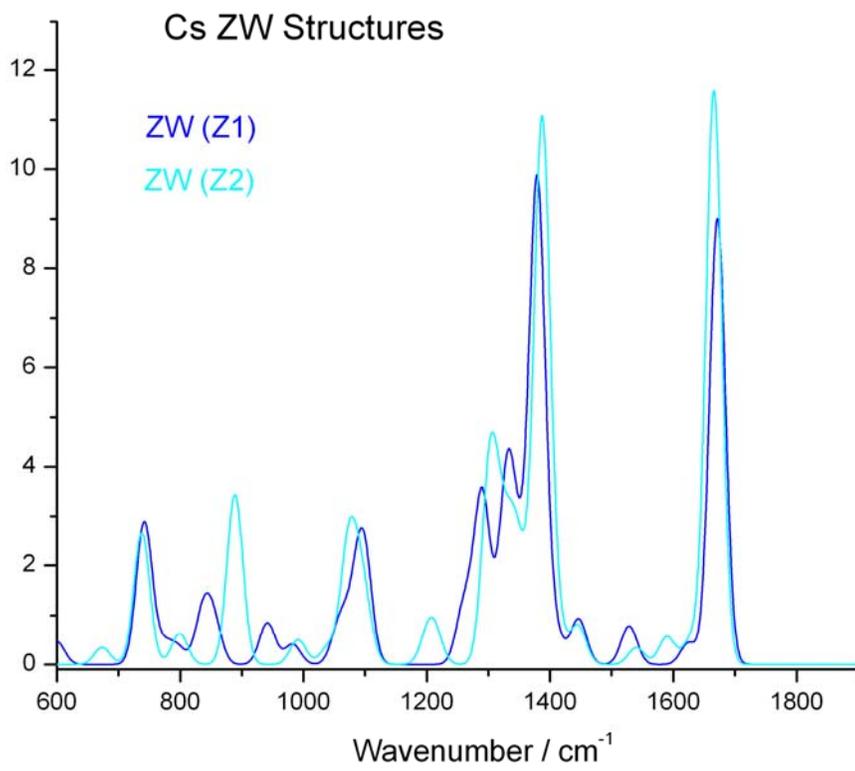
3. Salt-bridge (zwitterion) structures

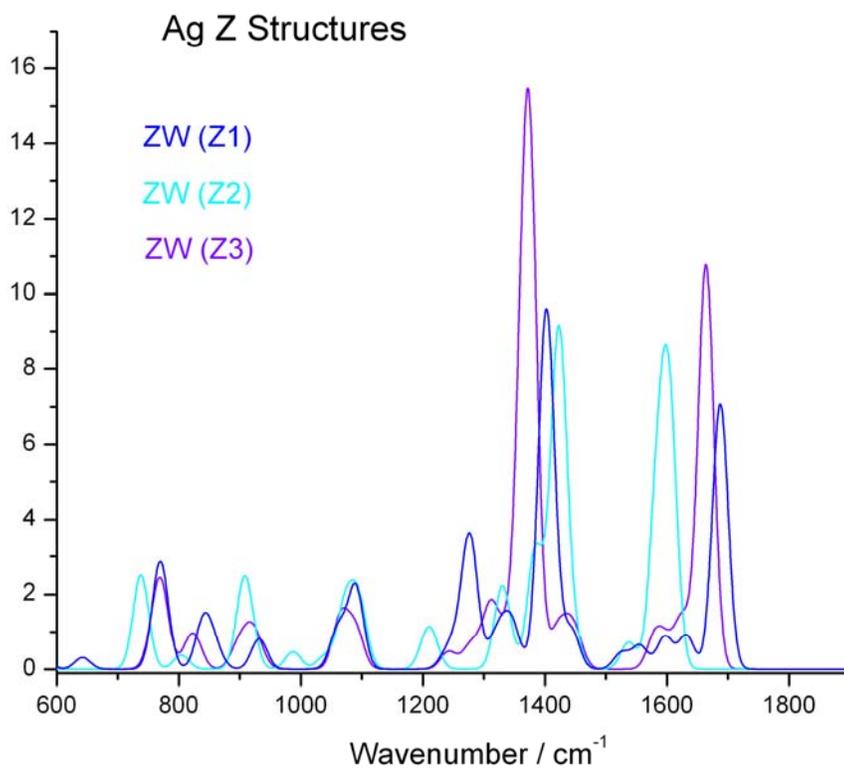




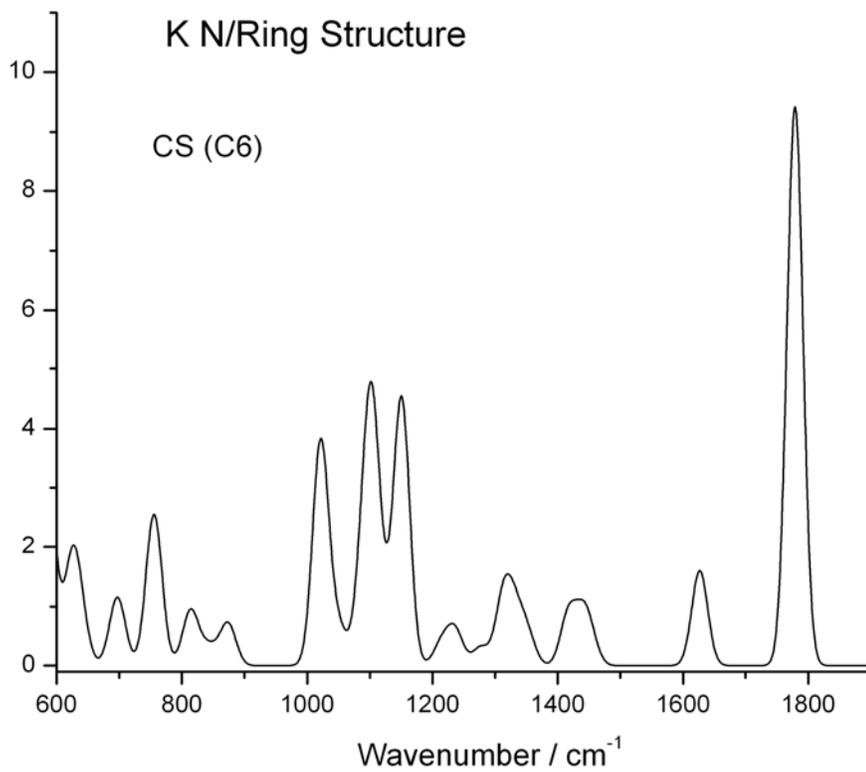


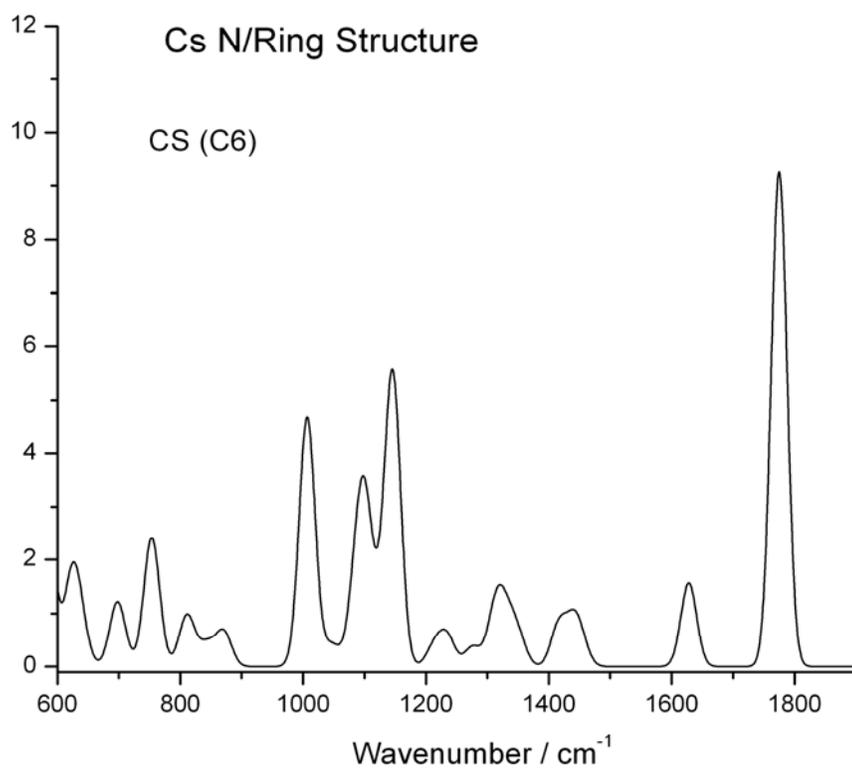


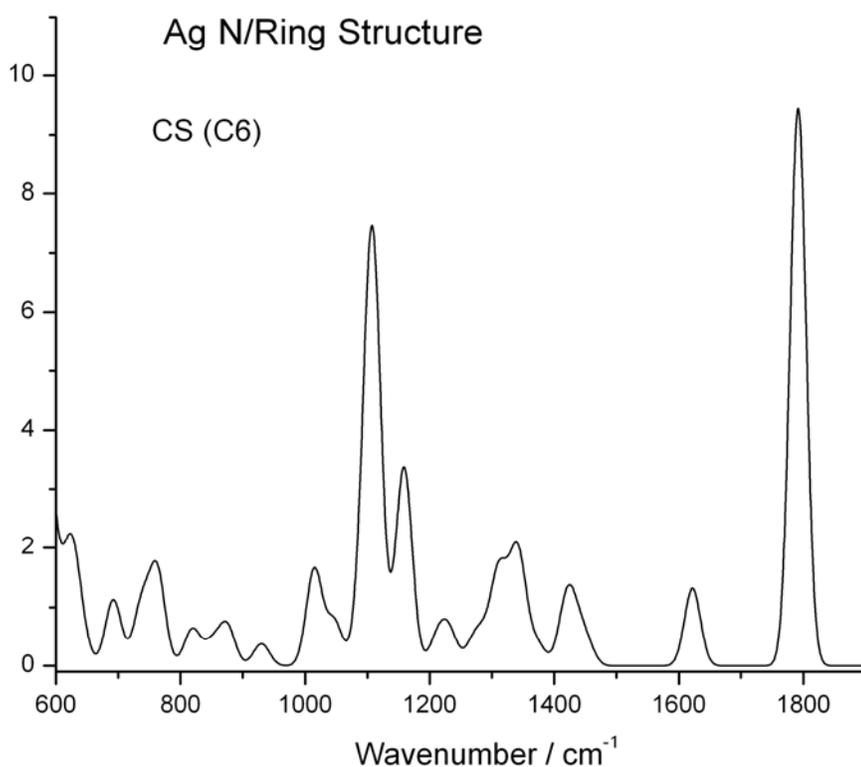




4. N/Ring structures







Further discussion of structural variants.

The most stable variation of the N/Ring binding motif was calculated for three metal ions. The energies are shown in Tables S1 and S2, and the predicted IR spectra are shown above. As Table S1 indicates, these isomers are substantially disfavored thermochemically relative to the most stable isomers, and would not be likely components of the populations, as is borne out in the spectra. In the cases of K^+ and Cs^+ , representing larger metal ions, the prominent observed peak near 1400 cm^{-1} has no corresponding strong peak in the predicted N/Ring spectra, and the fit is in general poor. In the Ag^+ case, representing smaller metal ions, a reasonable match of experimental and

predicted spectra is possible, but only if both of the intense peaks observed near 1730 and 1150 cm^{-1} are displaced by large increments of the order of 50 cm^{-1} . This seems unlikely, and is considered much less attractive than our assignment of this spectrum to the much more stable N/O/Ring isomer. Note also that the conversion of an N/Ring isomer into a much more stable N/O/Ring isomer is easily accomplished by a simple rotation of the side-chain, and should have no major barrier. Thus the N/Ring isomers are not considered to be important in these systems based on both spectroscopic and thermochemical considerations.

The C3 variant of the N/O/Ring binding motif differs from the other variants in that the OH hydrogen is rotated so that it has no hydrogen-bonding interaction with the carbonyl oxygen. Table S1 shows that this rotational variation costs about 24 kJ mol^{-1} in energy. The figures all show a similar effect of this variation, which shows up primarily in the large blue shift of the O-H bending vibration from $\sim 1150 \text{ cm}^{-1}$ to $\sim 1250 \text{ cm}^{-1}$. Looking at the experimental spectra in Fig. 1, we see that there is little or no intensity in the 1250 cm^{-1} region, so that there is no possibility of a significant presence of this variant in the populations. The other two N/O/Ring variants, C1 and C2 (in which the N and O ligands are exchanged), are not very different in energy, and are very similar spectroscopically, and we would not rule out the presence of some of the C2 variant. Similarly, the two O/Ring variants C4 and C5 are not very different in energy and are spectroscopically similar, so that we cannot be sure which of these is actually dominant in cases where this binding motif is present.

The Z2 salt-bridge variant differs from the other two SB variants in having no interaction between the metal and the side chain. This makes little difference thermochemically or spectroscopically for the alkalis, with this variant being quite similar

to the side-chain-chelated Z1 variant. The only interesting difference is the appearance of a predicted moderate-intensity peak near 900 cm^{-1} for the Z2 variant, which does not appear in the observed spectra. For Ag^+ , where metal-ion interaction with the ring is intrinsically stronger, the metal/side-chain interaction present in Z1 and Z3 makes these variants more stable than Z2, and also leads to a significant red shift of the carboxylate stretching vibration in the 1600 cm^{-1} region. However, this predicted peak in the Z2 variant of the Ag^+ complex is in even worse agreement with the observed spectrum than for the Z3 variant that was ruled out in the previous discussion, and it is certainly not a major contributor to the population.