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and other groups by 1,2 shifts in arenium ions have long been known to take place with great ease. While the ortho (**15**, **19**) and para (**17**) methoxybenzenium ions should be more stable than the meta isomers (**16**, **18**), migration via **18** may well not require too much energy. In any case the combination of **10** with methanol to form **14** must be very exothermic.

To test this mechanism, we have carried out detailed MIN-DO/3[16] calculations. We first confirmed the quoted[10,11] difference in energy (44 kcal/mol.) between **4** and **5** because no details had been published. Next we carried out calculations for the isomers **20–23**, obtained by protonating anisole in various positions. Their
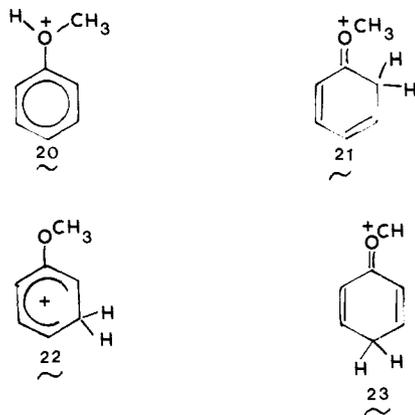
heats of formation and the corresponding proton affinities are shown in Table I, with values for methanol and benzene for comparison. Finally we calculated minimum-energy reaction paths (MERP) for the interconversions of **20–23**. The results are shown schematically in Figure 1.

The addition of methanol to **5** is extremely exothermic (ΔH_{calcd}–45 kcal/mol). In solution, however, this excess energy will be lost very rapidly. Since the barrier to rearrangement of **21** is quite large (26 kcal/mol) and since methanol is a stronger base than anisole in the liquid phase, the proton will be lost from **20** or **21** before it has time to migrate further. Consequently the sole product from **6** in methanol solution is **7**. In the gas phase, however, methanol is a weaker acid than anisole (Table I), and the excess energy of **20** will not be dissipated nearly so fast. It is therefore not at all surprising that tritium migration occurs. However, since migration of tritium involves a number of consecutive 1,2 hydrogen shifts, including at least three crossings of the intervening energy barriers (Figure 1), and since in each of the relevant steps there will be a large kinetic isotope effect favoring migration of hydrogen over that of tritium, it is unlikely that equilibrium will be achieved. The proportion of para isomer (**7**) is therefore likely to be much greater than that corresponding to equilibrium, i.e., **7/8/9** = 1:2:2. Since **19** is formed via **18**, the ratio of **8/9** should also be greater than the equilibrium value (1:1) but the difference should be less because the barrier between **18** and **19** is low. The products would then be expected to be formed in the order **7** ≫ **8** > **9**, as in fact was observed.

Our suggested mechanism could be tested very easily by submitting pure **7** (formed in liquid methanol) to a source of protons in methanol in the gas phase under the conditions used in the reaction of **6**.

Registry No. 4, 38815-08-6; **5**, 17333-73-2; **6**, 73728-29-7; **7**, 34650-00-5; **8**, 81617-35-8; **9**, 81617-36-9; **18**, 81643-51-8; **19**, 81643-52-9; **20**, 18223-09-1; **21**, 81617-37-0; **22**, 81643-53-0; **23**, 81617-38-1.

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Solid-State 13C NMR Characterization of the Bonding Mode of the Thiocyanate Ion in Copper(I) Complexes

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The ability of the thiocyanate ion to function as an ambidentate ligand has been the topic of considerable synthetic and structural investigations for over 20 years.[1] A wide variety of spectroscopic techniques have been applied to determine S vs. N bonding in thiocyanate complexes, including infrared,[1] Raman,[1] and X-ray photoelectron spectroscopy.[2] Two elegant magnetic resonance techniques were recently introduced by Fultz et al.[3,4] involving NQR and Kargol et al.[5] involving solution-state 13C NMR.

Kargol et al.[5] have shown that the 13C shift of the thiocyanate ligand is diagnostic of its bonding mode. In most cases examined by these authors, the S- and N-bound thiocyanate signals in the solution state are shifted to the higher- and lower-field side of ionic thiocyanate, respectively. We report here preliminary solid-state high-resolution 13C NMR results for two Cu(I) complexes that demonstrate that analogous structural assignments can be made in the solid state by using cross-polarization magic-angle spinning (CP/MAS). The experiments were performed on a multinuclear solid-state NMR spectrometer designed and built in-house.[6] An interrupted decoupling sequence, first suggested by Opella and Frey,[7] was used to suppress signals from protonated carbons. All compounds studied were ca. 90% enriched in [13C]SCN−. The contact times (5 ms) were somewhat longer than typical (1–2 ms), since no protons are located in the immediate vicinity of the thiocyanate ion.

Figure 1a shows the spectrum of potassium thiocyanate taken with conventional pulsed FT NMR and magic-angle spinning. A sharp line (<10 Hz) is observed, with no evidence of 14N quadrupole-induced splittings[8,9] and a remarkably short 13C relaxation time (~3 s). The 13C spectrum of [13C]KSCN without spinning is shown in Figure 1b. Again, quite surprisingly, a narrow (~10 ppm) and only slightly anisotropic line is observed. Taken together, the data indicate that the SCN− ion in solid KSCN is undergoing fast rotational and/or translational motion. The chemical shift of the SCN− ion is 134 ppm downfield from Me4Si, with the Delrin spinner signal taken to be at 90 ppm. This value is (coincidentally) identical with the chemical shift of the thiocyanate ion observed in aqueous KSCN solution.[5]

The bonding mode of the thiocyanate ligand was studied in the complexes CuL(CNS)[10] [L = CH3C(CH2PPh2)3 (I), PhP-(CH2CH2PPh2)2 (II)]. Infrared and 1H NMR studies of I have shown that this complex contains both Cu–SCN and Cu–NCS linkages in the solid state but exclusively Cu–NCS bonding in solution.[11]

(1) This subject is most recently reviewed in Burmeister (Burmeister, J. L. In "Chemistry and Biochemistry of Thiocyanic Acid and Its Derivatives"; Newman, A. A., Ed.; Academic: London, 1975; pp 68–130.

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(10) The designation of the thiocyanate ligand as CNS indicates an indefined bonding mode; NCS and SCN indicate nitrogen (isothiocyanate ligand) and sulfur (thiocyanate) bonding, respectively.

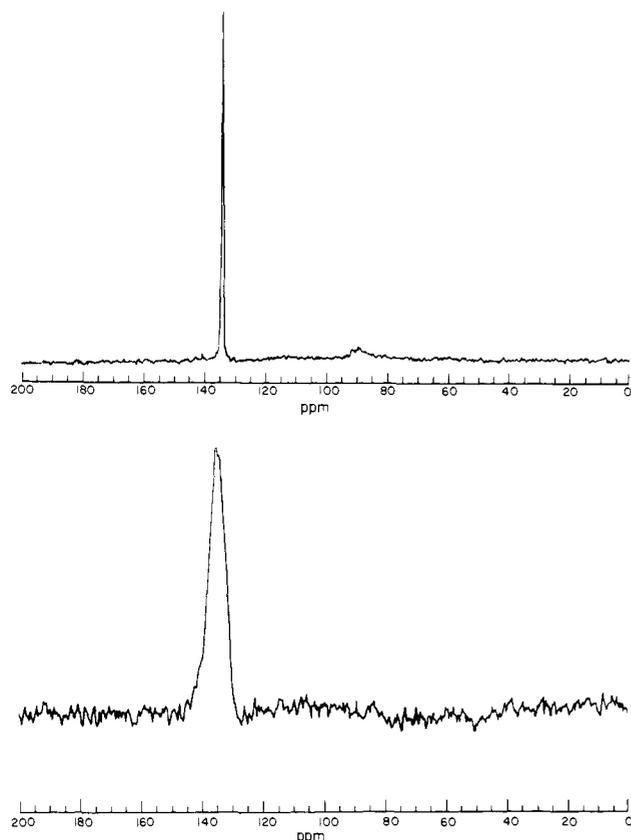(11) Gysling, H. J.; Gerenser, L. J.; Mason, M. G. *J. Coord. Chem.* **1980**, *10*, 67.

Figure 1. (a) ^{13}C FT NMR spectrum of solid [^{13}C]KSCN (200 mg) with magic-angle spinning (36 scans with 10-s repetition rate and 10-Hz line broadening). (b) ^{13}C spectrum of the same sample as in a without spinning.

A single-crystal X-ray diffraction study of this complex has confirmed the proposed solid-state structure.[12] The ^{13}C CP/MAS spectrum of I with ^{13}C-enriched thiocyanate ligand is shown in Figure 2. Two signals with distinctly different line widths are observed. The signal at higher field has a chemical shift (127 ppm) close to those of other S-bound thiocyanates in octahedral and tetrahedral complexes reported by Kargol et al.[5] (125–128 ppm). Similarly, the sharper low-field signal at 136 ppm falls within the range of chemical shifts typical of N-bound thiocyanate (135–146 ppm).

Cu(NCS)[PhP(CH$_2$CH$_2$PPh$_2$)$_2$] (II) is exclusively N-bound in both the solid state and in solution, as shown by infrared spectroscopy. The solid-state structure has been confirmed by a single-crystal X-ray diffraction study.[12]

The CP/MAS spectrum of II is shown in Figure 3. It displays a doublet with a splitting of 93 Hz due to the residual dipolar interaction with the quadrupolar ^{14}N nucleus.[8,9] The weighted
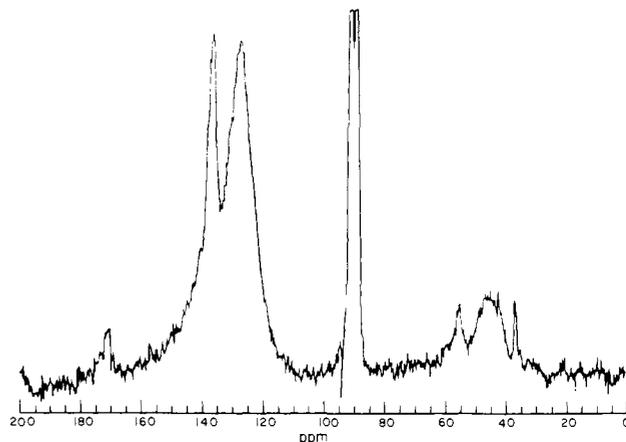
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Figure 2. Solid-state ^{13}C CP/MAS spectrum of solid [Cu(CH$_3$C-(CH$_2$PPh$_2$)$_3$)(CNS)] (average of 1000 transients, contact time 5 ms, decoupling interrupted for 120 μs before data acquisition).
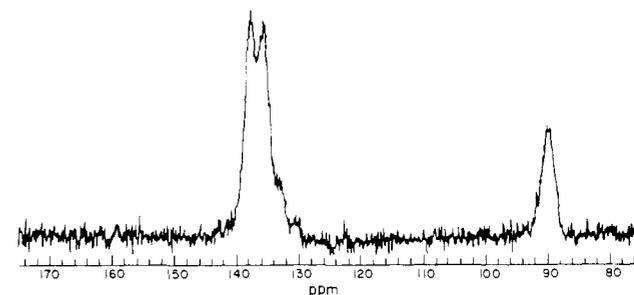

Figure 3. Solid-state ^{13}C CP/MAS spectrum of solid [Cu(PhP-(CH$_2$CH$_2$PPh$_2$)$_2$)(NCS)] (average of 152 transients, 1-Hz line broadening, other conditions as in Figure 2).

chemical shift of the doublet at 137 ppm is again wholly consistent with N bonding. Furthermore, for II, the ^{14}N nuclear quadrupole coupling constant can be estimated from the resolved splitting. From the C–N bond distance in the thiocyanate ligand (1.145 Å)[12] and the symmetry of the complex, one can calculate a nuclear quadrupole coupling constant of $\sim$1 MHz, using the methods outlined in the literature.[7,8] The estimated quadrupole coupling constant is less than 1.6 MHz, as predicted by the work of Fultz et al.[3] for N-bound thiocyanate.

In conclusion, we have shown that ^{13}C magic-angle spinning NMR is a convenient technique for establishing the bonding mode of the ambidentate thiocyanate ligand in the solid state.

The limitations of infrared spectroscopy, the most commonly used method in such assignments, have been pointed out by MacDougall et al.[13] The solid-state NMR method should also apply where the NQR method[5] fails because of excessively short proton spin-lattice relaxation times.

Further work on other thiocyanate complexes and variable-temperature studies in solid KSCN are under way in our laboratory.