

Copper-63 NMR Line width Study of the Copper(I)–Acetonitrile System

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The principal focus of this study is the ^{63}Cu NMR line widths in Cu(I)–acetonitrile (AN) solutions. The variations with the concentrations of Cu(I) salts (trifluoromethanesulfonate and perchlorate), added salts, water, chloride ion, and temperature have been studied. A quantitative analysis shows that the anomalous temperature dependence of the line widths is not due to ion pairing or anion complexation but results primarily from formation of a species with a different coordination number or less symmetrical arrangement of AN ligands than in the normal tetrahedral $\text{Cu}(\text{AN})_4^+$ ion. Solvent viscosity and ion pairing (with triflate) also are identified as factors having the expected effects on the line widths. The results of earlier studies also are discussed and analyzed by the current model where possible.

Introduction

Various salts of tetrakis(acetonitrile)copper(I) are widely used as starting materials in Cu(I) chemistry. The same salts dissolved in acetonitrile (AN) also are often used as line width benchmarks and shift standards in $^{63/65}\text{Cu}$ NMR studies. The present study began as an exploration of the possibility of using ^{63}Cu (I) NMR to measure the Cu(I)/Cu(II) electron-exchange rate in acetonitrile. Preliminary studies found that the trifluoromethanesulfonate (triflate) salts of Cu(I) and Cu(II) have advantageous solubilities in acetonitrile that would permit the widest concentration range for both in the electron-exchange studies. As a consequence, a major concern here is the NMR behavior of $\text{Cu}(\text{AN})_4$ (triflate) which had not been studied previously. The perchlorate salt also has been studied for comparison purposes. In addition, the effects of chloride ion and water on the ^{63}Cu (I) line widths have been examined.

A major problem with ^{63}Cu (I) NMR in AN is that the line is unusually broad so that the sensitivity is seriously affected. Two early studies^{1,2} have shown that the temperature dependence of the line width is anomalous in that it shows a minimum at about $-5\text{ }^\circ\text{C}$ and then broadens as the temperature increases through the ambient temperature region. As a result, the line width at $\sim 25\text{ }^\circ\text{C}$ is much greater than would be predicted from extrapolation of low-temperature line widths. The decrease in line width with increasing

temperature is expected for quadrupolar relaxation, as described in a following paragraph, but the cause of the increasing line width above $-5\text{ }^\circ\text{C}$ remains unexplained. The earlier studies suggested that this effect might be due to a coordination change¹ or to ion pairing.² One goal of this study was to seek a quantitative explanation for this anomaly, with the hope that it might then be possible to find conditions to minimize it and thereby improve the sensitivity, and also to add to the understanding of the coordination chemistry of the Cu(I)AN system and provide speciation information that might be critical for electron-exchange studies.

Results that may be relevant to the AN system have been reported by Marker and Gunter.³ They studied the complexes of Cu(I) with trimethyl and triethyl phosphite in CD_2Cl_2 and CDCl_3 and found a temperature dependence of the ^{63}Cu line widths (100–700 Hz) analogous to that observed in the AN system, with a minimum in the $0\text{--}20\text{ }^\circ\text{C}$ range. The phosphite systems have the advantage that both ^{63}Cu and ^{31}P NMR can be done and Cu–P coupling is observed in the ^{63}Cu and ^{31}P spectra. The authors interpreted the higher temperature behavior as due to ligand exchange with activation energies in the range of $\sim 4\text{ kcal mol}^{-1}$.

Since $\text{Cu}(\text{AN})_4^+$ is such a common standard in ^{63}Cu NMR studies, there have been a number of reports of line widths, and they are summarized in Table 1. Aside from a few strange results, such as the most recent on BF_4^- , and the earliest on PF_6^- , the reported values commonly fall in the 480–550 Hz range. However, there are several, including those from this study, in the 400–440 Hz range. Taken overall, the range of $\sim 150\text{ Hz}$ seems unexpected for materials

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Table 1. ⁶³Cu Line Widths of Cu(AN)₄X Salts in Acetonitrile

X ⁻	W _{1/2} , Hz	date	conditions ^a	ref
BF ₄	540	1978	0.1 M, Bruker SXP, 10 mm	c
BF ₄	490	1980	0.1 M, Varian XL-100, 10 mm	d
BF ₄	540	1982	0.087 M, Bruker SXP, 10 mm	e
BF ₄	600	1987	1.0 M, Varian FX-270, 30 °C	f
BF ₄	8570	1988	saturated (?), Bruker WH-200	g
PF ₆	800	1980	0.1 M, Varian XL-100, 10 mm	d
PF ₆	400	1983	saturated (?), Nicolet NT-360	h
ClO ₄	522 (494, T ₁) ^b	1980	0.1 M, Varian XL-100, 10 mm	d
ClO ₄	550	1982	0.061 M, Bruker SXP, 10 mm	e
ClO ₄	580	1982	0.10 M, Bruker SXP, 10 mm	e
ClO ₄	500	1984	1.05 M, JEOL FX-200, 10 mm	i
ClO ₄	505 (481, T ₁) ^b	1990	0.02–0.06 M, Bruker AM-400	j
ClO ₄	480	1995	0.05–0.065 M, Bruker AM-400	k
ClO ₄	480	1998	0.064 M, Bruker-500, 10 mm	l
ClO ₄	480	1999	0.064 M, Bruker-500, 10 mm	m
ClO ₄	440	1999	0.1 M, Bruker MSL-300	n
ClO ₄	520	2001	0.064 M, Bruker-300, 10 mm	o
ClO ₄	443	2002	0.062 M, Varian S-400	p
ClO ₄	423	2002	0.0062 M, Varian S-400	p
F ₃ CSO ₃	417	2002	0.00494 M, Varian S-400	p
F ₃ CSO ₃	463	2002	0.062 M, Varian S-400	p
F ₃ CSO ₃	460	2002	0.061 M, Bruker AM-200	p
F ₃ CSO ₃	488(492, T ₁) ^b	2002	0.117 M, Varian S-400	p

^a Temperatures are 25 °C unless stated otherwise, although sometimes not given. Sample tube diameter is 5 mm unless otherwise indicated. ^b A measured T₁ converted to the equivalent in Hz. ^c Reference 4. ^d Reference 1. ^e Reference 2. ^f Endo, K.; Yamamoto, K.; Deguchi, K.; Matsushita K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2803. ^g Connor, J. A.; Kennedy, R. J. *Polyhedron* **1988**, *7*, 161. ^h Reference 10. ⁱ Kitagawa, S.; Munakata, M. *Inorg. Chem.* **1984**, *23*, 4388. ^j Reference 6. ^k Reference 7. ^l Reference 8. ^m Gill, D. S.; Singh, L. J.; Singh, R.; Zamir, T.; Quickenden, L. *Ind. J. Chem.* **1999**, *38A*, 913. ⁿ Szlyk, E.; Szymanska, I. *Polyhedron* **1999**, *18*, 2941. ^o Reference 9. ^p Present study.

that are relatively easy to prepare and handle and are considered as standards. The range of line widths does not seem to be a function of advancements or differences in instrumentation. In seeking an explanation for this variation, the effects of sample size and spinning, and of possible common contaminants, also have been examined in this study.

Results

There have been several systematic studies of concentration and temperature effects on the line widths of ⁶³Cu(I) salts in acetonitrile by Ochsenbein and Schläpfer¹ and Kroneck et al.² Some representative results of temperature and concentration effects from this and the earlier studies are shown in Figures 1 and 2. The present results with the triflate and perchlorate salts are qualitatively similar to those obtained previously in that the line width shows a minimum at about –5 °C and increases with increasing concentration of the Cu(I) salt. The triflate salt gives slightly broader lines than the perchlorate. Although the trends are similar, there are considerable differences in the line widths of the perchlorate salt between the present and an earlier study.²

For ⁶³Cu with nuclear spin $I = 3/2$ and magnetogyric ratio $\gamma = 7.097 \times 10^7 \text{ s}^{-1} \text{ T}^{-1}$, nuclear relaxation is expected to be dominated by the quadrupolar relaxation mechanism and to be in the extreme narrowing limit. The latter requires that the nuclear precession rate times the correlation time for molecular tumbling (τ_Q) should satisfy the condition $(\pi\nu_0\tau_Q)^2$

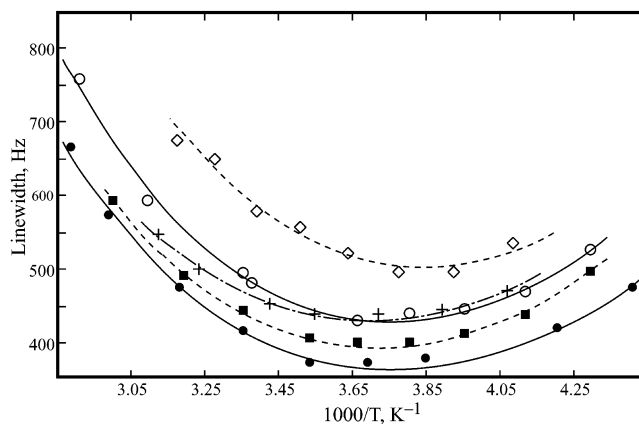


Figure 1. Temperature dependence of the ⁶³Cu(I) line width for Cu(AN)₄X salts in AN: X = ClO₄⁻ (◇) 0.10 M, ref 2, (■) 0.0621 M, this work; X = BF₄⁻ (+) 0.10 M, ref 1; X = triflate (●) 4.94×10^{-3} M, (○) 0.117 M, this work.

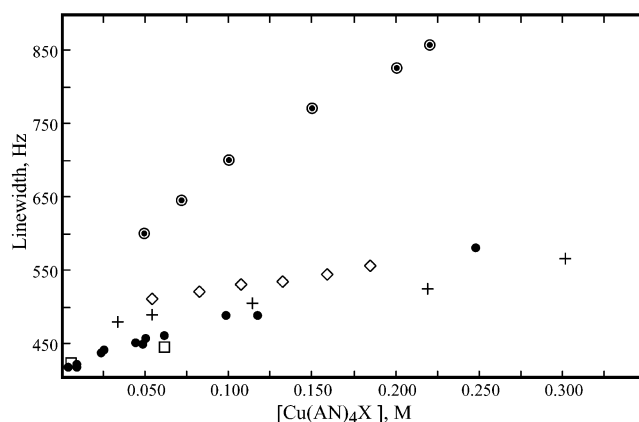


Figure 2. Concentration dependence of the ⁶³Cu(I) line width for Cu(AN)₄X salts in AN: X = ClO₄⁻ (◇) ref 2, (□) this work; X = BF₄⁻ (+) ref 1; X = triflate (●) this work; X = PF₆⁻ (○) ref 1.

$\ll 1$. For ⁶³Cu on a 400 MHz ¹H spectrometer, $\pi\nu_0 = 3.3 \times 10^8 \text{ s}^{-1}$ and $\tau_Q \leq 5 \times 10^{-11} \text{ s}$ for species such as Cu(AN)₄⁺ in a normal fluid, so that the extreme narrowing condition should be applicable. Then, the quadrupolar relaxation rate is given by eq 1

$$\frac{1}{T_2} = \pi W_{1/2} = \frac{3(2I + 3)}{40\{I^2(2I - 1)\}} \left(1 + \frac{\eta^2}{3}\right) \left(\frac{2\pi e^2 qQ}{h}\right)^2 \tau_Q \quad (1)$$

where $W_{1/2}$ is the full-width at half-height, η is the asymmetry parameter, and τ_Q is the correlation time. It is common practice to group the last two terms in brackets in the equation together as an effective quadrupole coupling constant (QCC), and eq 1 simplifies to eq 2.

$$\frac{1}{T_2} = \pi W_{1/2} = \frac{3\pi^2(2I + 3)}{10\{I^2(2I - 1)\}} (\text{QCC})^2 \tau_Q = 3.9478(\text{QCC})^2 \tau_Q \quad (2)$$

Quadrupolar relaxation is consistent with the line widths of ⁶³Cu(I) and ⁶⁵Cu(I) determined by Lutz and co-workers.⁴ The ratio of the line widths (540/470 = 1.149) is in reasonable agreement with the square of the nuclear qua-

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drupolar coupling constants (1.1686).⁵ In the present study, similar measurements on 0.062 M Cu(I) perchlorate and triflate gave values of $443/380 = 1.166$, and $465/399 = 1.165$, respectively. The extreme narrowing condition is consistent with the observations of Ochsenein and Schläpfer,¹ Gill and co-workers,⁶ and the present study that T_1 and T_2 for Cu(I) in acetonitrile are essentially equal (see Table 1). However, the temperature dependence above -5 °C is anomalous because quadrupolar relaxation should show a simple decrease in line width with increasing temperature due to the shortening of the correlation time (τ_Q). It has been suggested that this effect might be due to a coordination change¹ or to ion pairing² in the higher temperature region.

In a series of studies, Gill and co-workers have examined the ⁶³Cu(I) line width at 25 °C as cosolvents are added to AN. The lines inevitably broaden with the addition of another solvent, and this is attributed primarily to the formation of mixed complexes, but the temperature dependence was not studied, and the anomaly was ignored. In 1995, Gill et al.⁷ suggested that the ⁶³Cu(I) line widths are so large because of the Sternheimer antishielding factor (γ_∞) which has a value of -17 and contributes a factor of $(1 - \gamma_\infty)$ to the electric field gradient. More recently, Gill, Byrne, and Quickenden⁸ used the Stokes–Einstein equation to calculate a correlation time of $\sim 4.5 \times 10^{-11}$ s, and a QCC ≈ 3.0 MHz for 0.064 M CuClO₄ in AN. Most recently, Gill and co-workers⁹ have calculated a correlation time of 1.39×10^{-11} s in AN and used this to estimate that QCC = 5.46 MHz.

Of the results in Figure 2, the observations of Ochsenein and Schläpfer¹ on the PF₆⁻ salt are clearly unique. The concentration dependence is much more dramatic with an overall change in line width of ~ 400 Hz compared to ~ 50 Hz for the other anions. The temperature dependence (not shown) also is anomalous with a minimum at ~ 10 °C versus -5 °C for the others, and with a much larger line width in the low-temperature limit. Caulton et al.¹⁰ have reported a line width of 400 Hz for a “nearly saturated” solution of Cu(NCCH₃)₄PF₆ at 25 °C, compared to ~ 850 Hz at 0.22 M reported by Ochsenein and Schläpfer. In the present study, 0.0613 M CuClO₄ containing 0.050 M (Me₄N)PF₆ was found to have a line width of 447 Hz, entirely consistent with other samples at the same total salt concentration. These anomalies suggest that the sample of Ochsenein and Schläpfer was contaminated in some way, and these results will not be included in the further analysis.

If the Cu(I)/AN system is to be described by a two species model, Cu(NCCH₃)₄⁺ and either an ion pair or another species of different coordination or symmetry, then there are some simple expectations for these results. First, in the low

concentration limit, all of the salts should give the same line width. However, extrapolated values from the earlier studies (Figure 2) on the BF₄⁻ and ClO₄⁻ salts are ~ 470 and ~ 490 Hz, respectively, while the present study gives much smaller values of ~ 415 and 420 Hz for the triflate and ClO₄⁻, respectively. Second, below -5 °C where the temperature dependence is that expected for quadrupolar relaxation, all of the curves in Figure 1 should converge to that expected for the Cu(NCCH₃)₄⁺ ion. This expectation does seem to be realized in Figure 1 for the ~ 0.1 M triflate, perchlorate (present study), and tetrafluoroborate salts,¹ and the other deviations might be due to concentration differences.

Viscosity Effects. The Stokes–Einstein relationship suggests that the correlation time $\tau_Q \propto \eta/T$, where η is the viscosity of the solvent, and many studies have shown that viscosity increases with salt concentration.¹¹ Then, the simplest explanation for the concentration effects would be that they are due to the increase in viscosity with salt concentration which causes τ_Q and hence $W_{1/2}$ to increase.

Gill and co-workers¹² studied the viscosity of CuClO₄ in AN and found that the variation of viscosity with concentration of CuClO₄ is given by $\eta = \eta_0(1 + A[\text{CuClO}_4]^{1/2} + B[\text{CuClO}_4])$ with $A = 1.76 \times 10^{-2}$ and $B = 0.77$ at 25 °C. The concentration dependence of the viscosity is similar to that of tetra(*n*-propyl)ammonium bromide studied by Nikam and Sawant¹³ and by Saha and Das,¹⁴ who also studied the temperature dependence of the viscosity for *n*-Pr₄NBr in AN. The data for *n*-Pr₄NBr suggest that the temperature dependence of B (15–45 °C) can be represented by $B = 0.77(1 + 4.0 \times 10^{-3}(298 - T))$ and A has no discernible temperature dependence, possibly because it makes a small contribution to the overall effect. The temperature dependence of the viscosity of pure AN was determined between -40 and 20 °C by Kanes¹⁵ and is given by $\eta_0 = 0.152 \exp(924.7/T)$. The concentration dependence for CuClO₄ from Gill and co-workers, and the temperature dependencies from Saha and Das, and Kanes, can be combined to estimate the viscosity of CuClO₄ in AN, with the assumption that CuClO₄ and *n*-Pr₄NBr have the same temperature dependence.

It is noteworthy that both the line widths (Figure 2) and the viscosity have an essentially linear dependence on concentration. Since all of the concentration studies have been done at 25 °C, it is convenient for purposes of comparison to analyze the data in terms of the reduced viscosity, η/η_0 , where η_0 is the viscosity of the pure solvent (3.41 mP (millipoise)) and η is the viscosity of the salt solution. If $W_{1/2} \propto \tau_Q$ and $\tau_Q \propto \eta/T$, then

$$\left(\frac{\eta_0}{\eta}\right)W_{1/2} = \frac{C_v \eta_0}{T} = (W_{1/2})_{0,T} \quad (3)$$

where C_v is a proportionality constant and $(W_{1/2})_{0,T}$ is the line width in the pure solvent at temperature T . If viscosity

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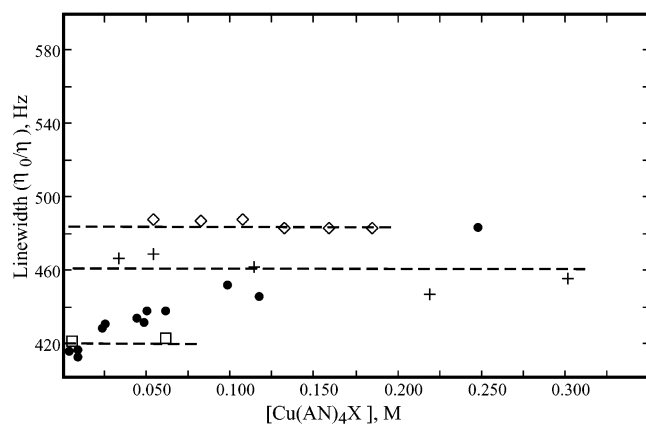


Figure 3. Concentration dependence of the ⁶³Cu(I) line width times reduced viscosity for Cu(AN)₄X salts in AN: X = ClO₄⁻ (◇) ref 2, (□) this work; X = BF₄⁻ (+) ref 1; X = triflate (●) this work. Dashed lines (---) are eyeguides only.

change is the only factor affecting the line width, then a plot of the factor $(\eta_0/\eta)W_{1/2}$ versus salt concentration should be a constant, independent of the salt concentration.

The appropriate plots are shown in Figure 3. The results suggest that $(\eta_0/\eta)W_{1/2}$ is essentially constant for the perchlorate and tetrafluoroborate salts, and that the concentration effect with these salts is primarily due to the viscosity change. The anomaly of different $(W_{1/2})_{0,T}$ values from different salts and sources remains. There appears to be a significant remaining effect of salt concentration on line widths for the triflate salt.

The apparently different behavior of triflate might be ascribed to quite different viscosity effects of the perchlorate and triflate anions, suggesting a much larger *B* value for the latter. But a rather large value of $B \approx 1.4$ is required to linearize the Cu(trif) (trif- = triflate) data. This seems unlikely from a comparison of the viscosities of sodium perchlorate and triflate in DMSO.¹⁶ The two salts show essentially the same concentration dependence in DMSO, and *B* values in AN and DMSO are generally of similar magnitude.¹¹ Results described later will show that there actually is a triflate ion effect on the line width which can be explained by ion pairing.

The viscosity/temperature dependence has been tested by comparing the temperature dependence of the ¹⁴N line widths in pure acetonitrile¹⁷ to those of a 0.045 M Cu(trif) solution. The results (Figure S1 in the Supporting Information) show that the viscosity corrected line widths of the Cu(trif) solution agree with those of the pure solvent, and both have the temperature dependence expected from the viscosity.

Water and Cu(II) Effects. Another possible explanation for the concentration dependence, and the different line widths with zero salt, is the presence of Cu(II) and/or adventitious water. The latter might be present in the solvent, or be introduced along with the salt. Water could act as a ligand in a lower symmetry complex and also would increase

Table 2. Water Dependence of ⁶³Cu(I) Line Width for Cu(AN)₄⁺ in AN

anion	[Cu(I)], M	AN, vol %	[H ₂ O], M	η , ^b cP	[Cu(II)], ^c mM	$W_{1/2}$, Hz	$W_{1/2}(\eta_0/\eta)$, Hz
BF ₄ ^a	0.087	100	0	0.363	0	540	508
BF ₄ ^a	0.10	99	0.51	0.365	0.099	560	522
BF ₄ ^a	0.10	98	1.08	0.370	0.196	620	573
BF ₄ ^a	0.10	95.25	2.64	0.393	0	805	699
BF ₄ ^a	0.10	95.25	2.64	0.393	0.476	850	716
BF ₄ ^a	0.10	95	2.78	0.395	0	900	777
BF ₄ ^a	0.10	90	5.61	0.440	0	1215	941
ClO ₄	0.062	100	0	0.356	0	443	422
ClO ₄ ^a	0.061	100	0	0.356	0	550	525
ClO ₄ ^a	0.089	91	5.04	0.428	0	2700	2152
ClO ₄ ^a	0.062	91	5.04	0.420	0.18	4800	3887
ClO ₄ ^d	0.064	100	0	0.403 ^e (0.36) ^f	0	520	(491)
ClO ₄ ^d	0.064		2.69	0.423 ^e	0	997	805
ClO ₄ ^d	0.064		5.36	0.440 ^e	0	1221	948
ClO ₄ ^g	0.061	90	5.61	0.429 ^b	0	1235	982
ClO ₄ ^d	0.064		14.5	0.627 ^e	0	2850	1552
ClO ₄ ^d	0.064		23.2	0.849 ^e	0	4300	1725
ClO ₄ ^d	0.064		28.3	0.977 ^e	0	5160	1800
ClO ₄ ^d	0.064		32.9	1.124 ^e	0	6400	1940
F ₃ CSO ₃ ^g	0.045	100	0	0.350	0	450	433
F ₃ CSO ₃ ^g	0.045		0.20	0.350	0	460	447
F ₃ CSO ₃ ^g	0.045		0.53	0.351	0	500	484
F ₃ CSO ₃ ^g	0.045		1.00	0.355	0	640	615

^a Reference 2. ^b Calculated from densities and viscosities compiled in ref 13 for AN/H₂O solutions. ^c The source of Cu(II) is not specified. ^d Reference 9 in AN/D₂O solutions. ^e Viscosities measured for the Cu(I)/AN/D₂O solutions. ^f Calculated value consistent with earlier CuClO₄/AN viscosity vs concentration results in ref 12. ^g Determined in the present study in AN/H₂O solutions.

the viscosity.¹³ This also might account for some of the variability between reported line widths noted in Table 1.

The effect of water has been examined in this study by preparing samples under vacuum and adding known amounts of water by dehydrating weighed amounts of [Co(NH₃)₅OH₂]-Br₃ at ~100 °C and condensing the water in the Cu(I)–AN solution in a dry ice slush. In addition, through a series of determinations of the density of various volume percentages of AN/H₂O, it has been possible to convert the earlier observations of Kroneck et al.² to water molarities for comparison to the present study. As part of the same study, Kroneck et al. also added Cu(II), at the submillimolar level to the solutions. These results are summarized in Table 2. It appears that the viscosity effect is not sufficient to account for the line width increases beyond [H₂O] > 0.5 M.

The results in Table 2 for the BF₄⁻ and F₃CSO₃⁻ salts are in agreement with regard to the trend with increasing [H₂O] and indicate a marked increase in line width for [H₂O] ≥ 0.5 M, with an essentially linear increase with [H₂O]. The somewhat larger line widths observed by Kroneck et al.² at lower [H₂O] might be due to water already present from the solvent and suggest that the [H₂O] ≈ 0.5 M, i.e., 99 vol % AN, in Kroneck's samples. The effect of Cu(II) with BF₄⁻ seems to be minor, but the ClO₄⁻ samples of Kroneck are anomalous in showing an apparently large Cu(II) effect, and more than twice the line width expected in 5.04 M water, compared to BF₄⁻. This anomaly is further shown by the fact that Gill's results for ClO₄⁻ are in good agreement with those of Kroneck for BF₄⁻, but not with the latter's ClO₄⁻ data.

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In the study of Kroneck et al.,² the temperature dependence of the line width for the ClO_4^- salt in 91% AN also is anomalous in showing a maximum at $\sim 30^\circ\text{C}$, while in pure AN there is a minimum at about -5°C . The authors² admit to having no explanation for this behavior. In the present study, the temperature dependence of 0.0613 M CuClO_4 in 90% AN/ H_2O was found to have a line width at 25°C in agreement with Gill et al.⁹ (see Table 2), and the temperature dependence was analogous to that in pure AN (see Figure S2 in Supporting Information). It appears that the sample of Kroneck et al.² was contaminated in some way.

It was noted previously that the PF_6^- sample of Schlöpfer had anomalously large line widths. If this was due to water in the sample, the sample would need to have been $\sim 5\text{ M}$ in H_2O , or $\sim 95\%$ AN. This would seem to be unlikely. It has been our observation that samples prepared in air from freshly opened acetonitrile as supplied by the manufacturer, and simply sealed with a plastic cap and Parafilm, show no effects of water in their NMR line widths.

Chloride Ion Effect. The variation in line widths observed by various workers might be caused by the presence of traces of potential ligands for Cu(I). Chloride ion is one of the more ubiquitous of such species, and its effect on the line widths has been investigated by adding $(\text{Et}_4\text{N})\text{Cl}$ to 0.0613 M CuClO_4 in AN. For chloride ion concentrations of 0.0015, 0.0031, 0.015, and 0.031 M, it was found that the ^{63}Cu line widths are 1089, 1874, 4370, and 7557 Hz, respectively, at 25°C . Clearly, even millimolar amounts of chloride ion have a large effect on the line width. These observations emphasize that traces of complexing anions can have very significant effects.

Line Width Temperature and Concentration Dependence Models. A simple two species model has been developed to model the Cu(I)/AN system. The species, **A** and **B**, are assumed to be in rapid equilibrium, as shown in eq 4.



Species **A** is expected to be $\text{Cu}(\text{AN})_4^+$ and is dominant at low temperatures, while **B** is a lower symmetry species with a larger line width and is favored at higher temperatures and concentrations. The reaction could be a simple structural change or involve the anion (X) to form an ion pair. The model also should give a rationalization for the observation that only triflate seems to show an appreciable concentration effect. In any case, if quadrupolar relaxation is dominant for both species, then the line width ($W_{1/2}$) and relaxation rate (T_2^{-1}) will be related to the species concentrations by eq 5

$$\pi W_{1/2} = T_2^{-1} = C_A^\circ \frac{[\mathbf{A}]}{[\mathbf{A} + \mathbf{B}]} \tau_{\text{QA}} + C_B^\circ \frac{[\mathbf{B}]}{[\mathbf{A} + \mathbf{B}]} \tau_{\text{QB}} \quad (5)$$

where C_A° and C_B° are temperature independent constants, and τ_Q is the correlation time governing the quadrupolar relaxation. If the Stokes–Einstein relationship is assumed, then $\tau_Q \propto \eta/T$, where η is the viscosity of the solvent, and

substitution into eq 5 and rearrangement gives eq 6.

$$\frac{\pi W_{1/2}}{\eta} = \left(\frac{T_2^{-1}}{\eta} \right) = \frac{C_A}{T} \frac{[\mathbf{A}]}{[\mathbf{A} + \mathbf{B}]} + \frac{C_B}{T} \frac{[\mathbf{B}]}{[\mathbf{A} + \mathbf{B}]} \quad (6)$$

The temperature dependence of the right-hand side of this expression depends only on the thermodynamic parameters, ΔH° and ΔS° , which characterize the **A** to **B** equilibrium. These parameters and the total concentration of Cu(I) and X can be used to calculate **[A]** and **[B]** and hence to fit the relaxation rate data as a function of temperature and concentration.

Concentration Dependence: Ion-Pair Model. The ion-pair model has been tested first because it seems the most natural way to account for the concentration dependence with F_3CSO_3^- . The lack of real concentration dependence with ClO_4^- and BF_4^- , beyond the viscosity effect already noted, could be ascribed to the low charge density and polarity of these ions compared to F_3CSO_3^- . Gejji et al. have considered the theoretical aspects of ion pairing of Li^+ , Na^+ , and NH_4^+ with F_3CSO_3^- in the gas phase.¹⁸ The Eigen–Fuoss¹⁹ model predicts that K_i might be in the range $1\text{--}5\text{ M}^{-1}$ for outer-sphere ion association between unit charged species in acetonitrile at 25°C .

For the Cu(I)–triflate solutions, a preliminary examination revealed that the line width increased nearly linearly with the concentration up to $\sim 0.05\text{ M}$. This suggests that the concentration of the ion pair is small relative to the total Cu(I) for such solutions, so that $K \leq 3\text{ M}^{-1}$. A visual analysis, with $K_i = 2$, produced a good fit of the data at 298 K for all the Cu(trif) solutions. It also was found that four solutions with $(\text{Bu}_4\text{N})(\text{trif})/\text{Cu}(\text{X})$ concentrations of 0.05/0.0613, 0.10/0.0613 ($\text{X} = \text{ClO}_4$), and 0.20/0.0624, 0.401/0.135 ($\text{X} = \text{trif}$) have line widths consistent with this model. However, solutions with Li(trif) added to $\text{Cu}(\text{ClO}_4)$ or Cu(trif) are not fitted as well, with line widths consistently smaller than predicted, and the Cu(trif) solutions have consistently larger line widths than corresponding solutions of $\text{Cu}(\text{ClO}_4)$. This suggests that the total triflate concentration does affect the line width, but the effective triflate ion concentration in Li^+ solutions is smaller than the expected value. One possible explanation for this is through ion pairing of Li^+ and F_3CSO_3^- . There have not been any studies relating to ion pairing of lithium triflate in AN, but Salomon and co-workers²⁰ have interpreted conductivity measurements to indicate $K_i = 18.4$ for $\text{Li}(\text{ClO}_4)$ in AN. Lithium triflate has been studied in butyrolactone,²¹ which has a dielectric constant similar to AN, and found to have $K_i \approx 20$.

In the final analysis, the model included the coupled equilibria for triflate ion pairing with Cu^+ and Li^+ , and the contributions of Cu^+ and the ion-pair $\text{Cu}\cdot(\text{trif})$ to the line

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Table 3. Triflate Ion Dependence of ⁶³Cu(I) Line Widths in AN

Cu(I) source	[Cu(I)] _{tot} mM	added salt mM	[trif] _{tot} mM	W _{1/2} , Hz ^a obsd	W _{1/2} , Hz ^a calcd
Cu(trif)	4.94	0	4.94	417	418
Cu(trif)	9.63	0	9.63	416	422
Cu(trif)	9.88	0	9.88	420 ^b	422
Cu(trif)	24.7	0	24.7	437	434
Cu(trif)	26.0	0	26.0	440 ^b	435
Cu(trif)	49.4	0	49.4	449	452
Cu(trif)	50.6	0	50.6	456	453
Cu(trif)	50.6	0	50.6	449 ^{b,f}	453
Cu(trif)	62.0	0	62.0	460 ^b	461
Cu(trif)	98.8	0	98.8	488	484
Cu(trif)	117.0	0	117.0	488	495
Cu(trif)	117.0	0	117.0	482 ^b	495
Cu(trif)	247.0	0	247.0	579	562
Cu(ClO ₄)	61.3	50.0 ^c	50.0	477	473
Cu(ClO ₄)	61.3	50.0 ^c	50.0	475	473
Cu(ClO ₄)	61.3	100.0 ^c	100.0	513	510
Cu(trif)	62.4	200.0 ^c	262.4	603	600
Cu(trif)	135.0 ^c	401.0 ^c	536.0	748	758
Cu(trif)	62.4	50.0 ^d	112.4	482	481
Cu(trif)	62.4	100.0 ^d	162.4	497	498
Cu(ClO ₄)	61.3	100.0 ^d	100.0	484	484
Cu(trif)	62.4	201.0 ^d	263.4	527	524
Cu(ClO ₄)	61.3	200.0 ^d	200.0	513	515
Cu(ClO ₄)	61.3	200.0 ^{d,e}	200.0	513	515
Cu(ClO ₄)	61.3	500.0 ^d	500.0	576	576

^a Measured on a Varian S-400 MHz spectrometer in 5 mm tubes unless otherwise indicated. ^b Measured on Bruker AM-200 MHz spectrometer. ^c Added as Bu₄N(trif). ^d Added as Li(trif). ^e Salt oven-dried immediately before sample preparation. ^f In 10 mm tube on Bruker AM-200.

width, while taking viscosity effects into account, using the parameters of Gill et al.¹² It was assumed that the viscosity *B* coefficient was the same for Cu⁺, Li⁺, and Bu₄N⁺, since the values are known to be quite similar.¹¹ The contributions of the ion pairs Cu•(trif) and Li•(trif) to the viscosity are problematic, and it was assumed that these neutral species did not make a significant contribution. Then, the line widths were fitted by least-squares to eq 7

$$W_{1/2} = \eta \left\{ \left(\frac{C_A}{T} \right) \frac{[Cu^+]}{[Cu(I)]_{tot}} + \left(\frac{C_B}{T} \right) \frac{[Cu \cdot trif]}{[Cu(I)]_{tot}} \right\} \quad (7)$$

where η is the viscosity in millipoise. The best fit gave K_i values for Cu⁺ and Li⁺ of 1.51 ± 0.48 and $9.0 \pm 1.3 \text{ M}^{-1}$, respectively, with $(C_A/T) = 1.213 \pm 0.007 \times 10^3$ and $(C_B/T) = 2.16 \pm 0.15 \times 10^3$.

The solution compositions and results for the ion-pair model study are summarized in Table 3. The excellent agreement between the observed and calculated line widths, and the quite reasonable magnitudes of the K_i 's seem to vindicate the model as an explanation for the concentration effects with triflate. It should be noted that the latter depend on the details of the viscosity correction, but similar values are obtained with any model assuming a normal dependence of viscosity on salt concentration.

Temperature Dependence. (a) Ion-Pair Model. The ability to explain the temperature dependence also is a critical requirement of any successful model. The Cu⁺–F₃CSO₃[–] ion-pair model assumes that there is more ion pairing at higher temperature in order to explain the increasing line widths above –5 °C. This implies in turn that there should be a more pronounced concentration dependence of the line

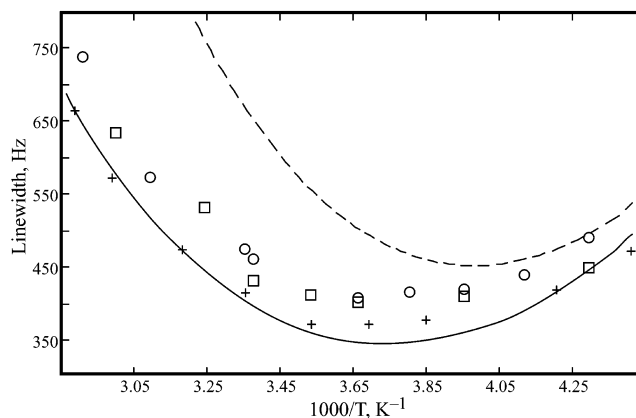


Figure 4. Temperature and concentration dependence of ⁶³Cu(I) line widths for Cu(AN)₄(triflate): (+) 4.94×10^{-3} M; (□) 4.5×10^{-2} M; (○) 0.117 M. Curve (—) calculated from the ion-pair model for 4.94×10^{-3} M, $K_i = 1.5$ (25 °C), $\Delta H^\circ = 6.0 \text{ kcal mol}^{-1}$, and $\Delta S^\circ = 20.93 \text{ cal mol}^{-1} \text{ K}^{-1}$. Curve (---) calculated for 9.88×10^{-3} M and the same ΔH° and ΔS° .

widths at higher temperature. The ΔH° for the ion-pair formation constant (K_i) will be determined essentially by the observed temperature dependence of the line widths.

To test the ion-pair model, the temperature dependences of 4.94×10^{-3} , 4.50×10^{-2} , and 0.117 M solutions of Cu(trif) in AN were studied. A qualitative examination of the line widths (Figure 4) reveals that there is not a marked sensitivity to concentration at higher temperature, and it would appear that this model may not work, unless the ΔH° is sufficiently small so that K_i does not change too much between 25 and 70 °C. Small K_i and ΔH° values also are suggested by the fact that the temperature of the minimum line width does not seem to shift much with concentration. Otherwise, one would expect the higher temperature arm to become more important at higher concentrations, and the minimum would shift to lower temperature.

For the analysis, the value of $K_i = 1.5$ at 25 °C was taken from the previous analysis, various ΔH° values (1–10 kcal mol^{–1}) were assumed, and the ΔS° was calculated. It was found that a ΔH° in the range 5–6 kcal mol^{–1} is required to reproduce the observed temperature dependence of the line widths. Such ΔH° values are clearly in conflict with the implication of the data that K_i does not change much from 25 to 70 °C. This was confirmed by model calculations based on fitting the lowest concentration data with $K_i = 1.5$ (25 °C), $\Delta H^\circ = 6.0 \text{ kcal mol}^{-1}$, and $\Delta S^\circ = 20.93 \text{ cal mol}^{-1} \text{ K}^{-1}$ (solid curve in Figure 4). If the same parameters are used to calculate the curve for twice the total Cu(trif) concentration (9.88×10^{-3} M) (dashed curve in Figure 4), the predicted line widths are much larger than those observed even in the 0.117 M solution. The calculated curve follows the expectations of increasing line width change at higher temperature and shift of the minimum to lower temperature, but it simply cannot reproduce the experimental observations.

The conclusion from this analysis is that the ion-pair model alone cannot account for the increase in line width with temperature. It can account for the small concentration effects, but the ion-pair formation constant must have a much smaller temperature dependence than the line widths.

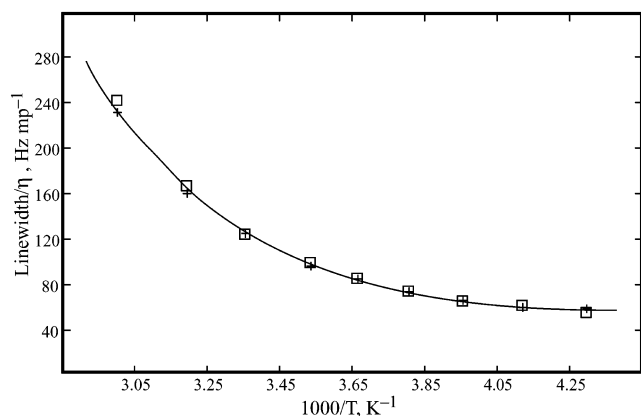


Figure 5. Temperature dependence of the $^{63}\text{Cu}(\text{I})$ line width divided by viscosity for $\text{Cu}(\text{AN})_4\text{ClO}_4$ in AN: (+) 6.21×10^{-2} M; (□) 6.21×10^{-3} M.

(b) Coordination Change Model. An alternative model assumes that **A** and **B** are related by some change in the coordinated ligands such that **B** is less symmetrical than **A** and therefore provides more effective quadrupolar relaxation. It should be noted that the minimal temperature dependence of the triflate concentration effect, already noted, shows that the coordination change does not involve formation of $\text{Cu}(\text{AN})_3(\text{trif})$. The concentration dependence is due in part to viscosity changes and to ion pairing but is relatively temperature independent compared to the coordination change equilibrium.

The perchlorate samples studied here present a good initial test for this model. The concentration dependence is consistent with viscosity effects, so that there are no complications with the magnitude or temperature dependence of ion-pair formation. Minor modification of eq 7 gives eq 8

$$\frac{W_{1/2}}{\eta} = \frac{1}{T} \left\{ C_A \frac{[\text{A}]}{[\text{A} + \text{B}]} + C_B \frac{[\text{B}]}{[\text{A} + \text{B}]} \right\} \quad (8)$$

where **A** and **B** are the symmetrical and less symmetrical species, respectively, and C_A and C_B are temperature independent constants dependent on the QCC for the respective species. The concentration and temperature dependence of the viscosity, η , can be calculated as previously described. In the low-temperature limit where $[\text{A}] \gg [\text{B}]$, a plot of $W_{1/2}/\eta$ versus $1/T$ should be linear with a slope of C_A . In the opposite limit, the slope would be C_B , but the data do not indicate that this limit is ever really reached for the accessible temperature range.

The appropriate plots for two samples of 6.21×10^{-3} and 6.21×10^{-2} M $\text{Cu}(\text{ClO}_4)$ are shown in Figure 5. The low-temperature limit is clearly observed, and the viscosity change adequately corrects for the concentration dependence. A nonlinear least-squares analysis gave an excellent fit of the data with $\Delta H^\circ = 5.4 \text{ kcal mol}^{-1}$, $\Delta S^\circ = 9.78 \text{ cal mol}^{-1} \text{ K}^{-1}$, $C_A = 1.125 \times 10^4$, and $C_B = 17.86 \times 10^5$. However, because the latter value is not defined by the data, it was necessary to hold ΔH° constant during the fitting, and the values given produce the minimum standard error of the fit for ΔH° in the range 4.5–8.0 kcal mol^{-1} . The curve in Figure

5 is calculated on the basis of the parameters given and shows that the model does fit the data.

Further justification for the model is difficult to provide because of the unknown nature of the lower symmetry species **B**. The ΔH° is similar to that found by Marker and Gunter³ for the $\text{Cu}(\text{I})$ –phosphite systems. The relative values of C_A and C_B should depend on the values of $(\text{QCC})^2$ for the two species, assuming that they have very similar correlation times. The ratio $C_B/C_A = 158$ suggests that **B** has a 12.6 times larger QCC than **A**.

The value of C_A can be used to estimate that $W_{1/2} \approx 128$ Hz for species **A** at 25 °C, and then, the most recent value of $\tau_Q \approx 1.4 \times 10^{-11}$ s, from Gill and co-workers,⁹ yields $\text{QCC}_A = 2.7$ MHz for $\text{Cu}(\text{AN})_4^+$. The only homoleptic tetrahedral $\text{Cu}(\text{I})$ species with a known QCC seems to be $\text{Cu}(\text{CN})_4^{3-}$, for which $\text{QCC} = 1.125$ MHz has been determined by Kroeker and Wasylshen.²²

The value of QCC_A and the ratio C_B/C_A gives $\text{QCC}_B \approx 34$ MHz for species **B**. Lucken and co-workers²³ have reported a number of NQR measurements for $\text{Cu}(\text{I})$ complexes, but they have more complex ligand systems than AN. For 3-coordinate $(2,6\text{-lutidine})_2\text{Cu}(\text{halide})$ complexes, the NQR frequencies are 33–38 MHz, while analogous $(2,6\text{-lutidine})_3\text{Cu}^+$ species are in the range 43–46 MHz. For several compounds of the general coordination type P_2CuS_2 and PCuS_3 , Asaro et al.²⁴ have determined quadrupole coupling constants from solid-state NMR in the range 17–27 MHz. Two linear bis(tribenzylphosphine) $\text{Cu}(\text{I})$ salts have QCC in the range of 80 MHz.²⁵ All that can be said is that a value of ~ 34 MHz for species **B** appears to be in the range of possible values.

The BF_4^- system previously studied by Ochsenbein and Schläpfer¹ and Kronek et al.² is analogous to the perchlorate in that there is no indication of ion pairing, so that the same parameters for K_C should describe the BF_4^- system. Plots of $W_{1/2}/\eta$ versus $1/T$ for these data are shown in Figure 6. The results of the two studies generally are in agreement between about -15 and 20 °C, but Kronek et al. reported larger line widths at higher temperatures and somewhat smaller values at lower temperatures. The curve through the data of Ochsenbein and Schläpfer in Figure 6 is drawn with essentially the same parameters as those for the perchlorate system, $C_A = 1.15 \times 10^4$ and $C_B = 17.9 \times 10^5$. However, the data of Kronek et al. require $C_A = 0.90 \times 10^4$ and $C_B = 21.6 \times 10^5$, which are $\sim 20\%$ lower and higher, respectively, than the others. These observations, combined with those for the triflate system described in following paragraphs, suggest that there is some systematic error in the observations of Kronek et al.

The temperature dependence for $\text{Cu}(\text{trif})$ is more complex to analyze because the ion-pairing equilibrium is coupled to

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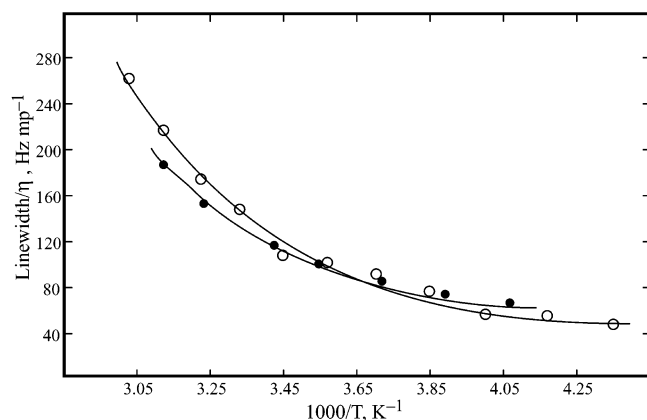


Figure 6. Temperature dependence of the ⁶³Cu(I) line width divided by viscosity for Cu(AN)₄BF₄ in AN: (●) 0.10 M, ref 1; (○) 0.09 M, ref 2.

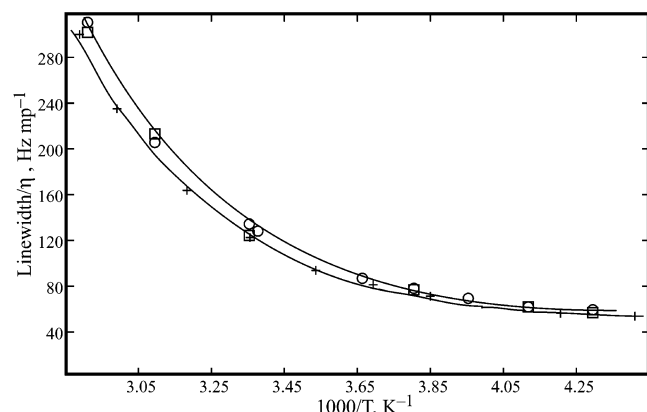
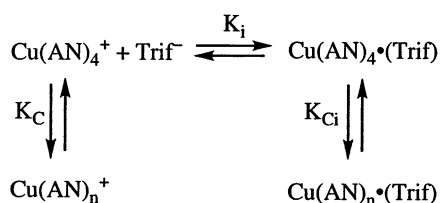


Figure 7. Temperature dependence of the ⁶³Cu(I) line width divided by viscosity for Cu(AN)₄(trif) in AN: (+) 4.94 × 10⁻³ M; (□) 9.88 × 10⁻³ M; (○) 0.117 M. The calculated curves for the first two solutions are indistinguishable.

Scheme 1



that for the coordination change. The plot of $W_{1/2}/\eta$ versus $1/T$, shown in Figure 7, is quite similar to that for the perchlorate system, aside from the slight changes with concentration. The results have been analyzed by solving the coupled equilibria in Scheme 1 for the four species, Cu(AN)₄⁺, Cu(AN)₄•(trif), Cu(AN)_n⁺, and Cu(AN)_n•(trif), where the latter two result from the coordination change.

The analysis of the perchlorate system has given K_C and its temperature dependence, and some indication of the ratio of the QCC values for Cu(AN)₄⁺ and Cu(AN)_n⁺. The triflate system has shown that $K_i = 1.5$ at 25 °C with a small temperature dependence, and it indicates that the ion pair causes ~1.8 times more broadening than its parent. However, nothing is known about K_{Ci} or the magnitude of QCC for Cu(AN)_n•(trif). Therefore, the simplest assumptions have been made in analyzing this system, namely that $K_{Ci} = K_C$ and that the broadening due to Cu(AN)_n•(trif) is 1.8 times

that for Cu(AN)_n⁺. Then, the contributions from the (AN)₄ species and from the (AN)_n species are given by F_4 and F_n , respectively.

$$F_4 = C_A([\text{Cu(AN)}_4^+] + 1.8[\text{Cu(AN)}_4 \cdot (\text{trif})]) \quad (9)$$

$$F_n = C_B([\text{Cu(AN)}_n^+] + 1.8[\text{Cu(AN)}_n \cdot (\text{trif})]) \quad (9)$$

The predicted line width divided by viscosity is given by eq 11

$$\frac{W_{1/2}}{\eta} = \frac{F_4 + F_n}{T[\text{Cu}]_{\text{tot}}} \quad (11)$$

where $[\text{Cu}]_{\text{tot}}$ is the total Cu(I) concentration.

The analysis of the results initially indicated that the ΔH° for K_i is <1 kcal mol⁻¹, and a value of 0.50 kcal mol⁻¹ has been used, along with $\Delta S^\circ = 2.48$ cal mol⁻¹ K⁻¹, to give $K_i = 1.5$ at 25 °C. For K_C , the thermodynamic parameters from the perchlorate system were used. The curves in Figure 7, which reproduce the data very well, were calculated with $C_A = 1.06 \times 10^4$ and $C_B = 17.9 \times 10^5$. The latter value is identical to that found to fit the perchlorate system, and the former is 6% smaller than for the perchlorate salt.

In theory, if the viscosity/concentration effect in both systems and the ion-pair effect with triflate have been correctly evaluated, then the two systems should give the same values for C_A and C_B . The agreement found gives substantial support for the generic, coordination-change model to explain the large ⁶³Cu line widths and their anomalous temperature dependence.

The question remains: what really is Cu(AN)_n⁺? The present study has established that it is not an ion pair, Cu(AN)_n•(X), and it is not the stoichiometrically equivalent inner-sphere complex, Cu(AN)₃(X). On the basis of the general coordination chemistry of Cu(I), a coordination number greater than 4 is very improbable. Then, one is left with Cu(AN)₃⁺ as the most likely possibility.

Experimental Section

Materials. Acetonitrile (Caledon, Fisher, or BDH) was dried over 4 Å molecular sieves for several days before use. Doubly distilled water was used whenever required. Diethyl ether (Fisher), perchloric acid (Fisher), trifluoromethanesulfonic (triflic) acid (Aldrich), cuprous oxide (Matheson, Coleman and Bell), cupric oxide (Fisher), and copper foil (Matheson, Coleman and Bell) were used as supplied. Tetraethylammonium chloride (Sigma), tetra(*n*-butyl)ammonium triflate (Aldrich), tetra(*n*-butyl)ammonium perchlorate (Aldrich), tetramethylammonium tetrafluoroborate (Aldrich), and tetramethylammonium hexafluorophosphate (Aldrich) were dried in an oven at 90 °C. Lithium triflate was prepared by adding ~5 M triflic acid to an aqueous slurry of the required amount of lithium carbonate (Fisher), concentrating the resulting clear colorless solution to dryness, and then washing the solid with diethyl ether and drying in vacuo.

Cu(OH)₂(O₃SCF₃)₂. A 1% excess of 5 M triflic acid was added to an aqueous slurry of cupric oxide (3.58 g, 25 mmol) at 60 °C and stirred until a clear blue solution remained. The solution was concentrated to dryness on a steam bath, and the remaining solid was dissolved in a minimum amount of acetonitrile, recrystallized

with ether, filtered, washed with ether, and dried in air. Anal. Calcd for $\text{Cu}_2\text{F}_6\text{H}_8\text{O}_{10}\text{S}_2$: Cu, 14.65; C, 5.54; H, 1.86. Found: Cu, 14.50; C, 5.20; H, 1.67.

$\text{Cu}(\text{O}_3\text{SCF}_3)_2$. The anhydrous material was obtained as a white, hygroscopic powder by heating the tetrahydrate in an oven at 100 °C for 3 days. Anal. Calcd for $\text{Cu}_2\text{F}_6\text{O}_6\text{S}_2$; C, 6.64. Found: C, 6.30.

Crystals obtained from a solution of the hydrated salt in dried acetonitrile are $\text{Cu}(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})_2(\text{O}_3\text{SCF}_3)_2$. Water-free crystals, $\text{Cu}(\text{CH}_3\text{CN})_4(\text{O}_3\text{SCF}_3)_2$, were only obtained when the anhydrous salt was used.

$\text{Cu}(\text{NCCH}_3)_4(\text{O}_3\text{SCF}_3)$. In a modification of a published procedure,²⁶ a mixture of acetonitrile (20 mL), $\text{Cu}(\text{H}_2\text{O})_4(\text{O}_3\text{SCF}_3)_2$ (2 g, 4.6 mmol), and copper foil (0.5 g, 7.9 mmol) was stirred in a capped parafilm-sealed Erlenmeyer flask until the solution turned colorless. Filtration on a 4–8 μm sintered glass frit gave a clear solution. The product was recovered as a white powder in two ways. The first method involved removal of the solvent by vacuum distillation. An ice/water slush was used to trap the solvent, and pumping was stopped just when the solid appeared to be reasonably dry. The use of a liquid nitrogen trap or prolonged pumping seemed to give a product that was more sensitive to air and moisture. The product was then transferred to a glovebag and stored under prepurified N_2 . In the second method, anhydrous diethyl ether was added to the solution and the white solid allowed to settle before collecting by filtration under argon. The product was dried and stored under argon. This product seemed more air-resistant than that from the vacuum distillation. A portion of product was dissolved in 0.1 M HClO_4 and analyzed for copper by the $\text{KI}/\text{S}_2\text{O}_3^{2-}$ method. Anal. Calcd for $\text{Cu}_9\text{F}_3\text{H}_{12}\text{N}_4\text{O}_3\text{S}$: Cu, 16.86; N, 14.87; C, 28.69; H, 3.21. Found: Cu, 17.10; N, 14.18; C, 27.64; H 2.98.

$\text{Cu}(\text{NCCH}_3)_4(\text{ClO}_4)$. A published procedure²⁷ was modified by adding a 1% excess of 70% (~11.6 M) perchloric acid to an acetonitrile slurry of cuprous oxide (1.43 g, 10 mmol) at 40 °C and stirring the mixture for 1 h. To the resulting colorless solution, a similar volume of diethyl ether was added, and the resulting white crystals were allowed to settle before collecting by filtration and washing with 80%/20% v/v ether/acetonitrile. This salt is stable in air for several months with no visible oxidation if moisture is excluded.

$(\text{NH}_3)_5\text{Co}(\text{OH}_2)\text{Br}_3$. A 1.0 g sample of $[(\text{NH}_3)_5\text{CoCO}_3]\text{NO}_3$ was added to a solution of 20 mL of water and 20 mL of concentrated HBr in an ice bath. The mixture was stirred for 10 min, and then, the solid product was allowed to settle before it was collected by filtration. The product was washed with ethanol and ether and air-dried.

NMR Samples. On the benchtop, stock solutions were made by quickly weighing and transferring the triflate or perchlorate salt to a measured volume of a $\text{CH}_3\text{CN}/\text{CD}_3\text{CN}$ mixture in a vial which

was then capped and covered with Parafilm. Aliquots of freshly prepared stock were diluted to obtain the required concentration. Samples of 0.6 mL (5 mm o.d. tubes) or 4 mL (10 mm o.d. tubes) were then transferred to the NMR tube which had been deaired by flushing with argon for 5 min. The argon was bubbled through the solution for a further 1 min before placing a septum cap and sealing with Parafilm. Other salts were added similarly to the $\text{Cu}(\text{I})$ solutions. These samples were routinely stored in a refrigerator. Samples also were prepared on a vacuum line by distilling $\text{CH}_3\text{-CN}/\text{CD}_3\text{CN}$ onto a weighed amount of $\text{Cu}(\text{NCCH}_3)_4(\text{O}_3\text{SCF}_3)$ in a weighed NMR tube. Then, the tube was sealed and reweighed to determine the final concentration. Samples containing small amounts of water were prepared on the vacuum line by collecting the water released from weighed amounts of $(\text{NH}_3)_5\text{Co}(\text{OH}_2)\text{Br}_3$ (heated at 100–110 °C)²⁸ onto the $\text{Cu}(\text{I})$ –acetonitrile sample in a dry ice slush. The tube was then sealed under vacuum and the composition determined from the mass as described.

$^{63,65}\text{Cu}$ NMR and ^{14}N NMR Measurements. The ^{63}Cu NMR spectra were recorded using broad band probe heads on Varian S 400 and Bruker AM 200 spectrometers. The latter also was used for the ^{14}N spectra. Samples were in 5 mm o.d. tubes, except for one ^{63}Cu measurement at 25 °C in a 10 mm o.d. tube on the Bruker system. Typical NMR parameters were the following: 45° pulse, delay $\sim 5T_1$, spectroscopic window 50 kHz, exponential filter (line broadening) 10 Hz. For the ^{63}Cu spectra, about 9500 scans (Bruker) or 1000 scans (Varian) were collected, while 400 scans were used for ^{14}N . The line widths were determined by fitting to a Lorentzian line shape using the spectrometer's software, as well as locally developed programs. Both methods were in good agreement. The variable temperature ^{63}Cu and a few ^{65}Cu (25 °C) NMR spectra were recorded on the Varian S 400. The T_1 was determined by a $(\pi-\tau-\pi/2-\text{Acq}-\text{D})n$ ($n = 1500$ transients at each of 11 τ values) sequence on 0.117 M $\text{Cu}(\text{NCCH}_3)_4(\text{O}_3\text{SCF}_3)$ and analyzed using the Varian software. In all line width measurements, it was observed, in agreement with Marker and Gunter³, that when an exponential filter was applied to the FID, the resultant line broadening needed to be subtracted to obtain the correct line width.

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Supporting Information Available: Figure S1 comparing the temperature dependence of the ^{14}N line widths of acetonitrile and a 0.045 M solution of $\text{Cu}(\text{trif})$ and Figure S2 showing the temperature dependence of the $^{63}\text{Cu}(\text{I})$ line widths of 0.0613 M $\text{Cu}(\text{ClO}_4)$ in 10% water, 90% acetonitrile. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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