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The stabilisation and characterisation by infrared spectroscopy of the different bonding modes of copper(I) thiocyanate adsorbed on high surface area solids

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Abstract

High surface area solids such as alumina, silica or charcoal, have been used to stabilise the various bonding modes of copper(I) thiocyanate. Infrared spectroscopy was used to characterise the different species, for example on alumina sulfur bonded, nitrogen bonded and bridged thiocyanate species were observed. The effect of the high surface area solid was in some cases dramatic and the bonding modes stabilised were found to be dependent upon the concentration of the impregnating solution, relative to the amount of high surface area solid present. The most striking differences were between charcoal and the other two solids, in the former case high loadings of copper(I) thiocyanate resulted in stabilisation of a bridged species, whereas only low loadings of copper(I) thiocyanate on alumina or silica resulted in stabilisation of a bridged thiocyanate species. Both nitrogen and sulfur bonded thiocyanate species were evident on all the supports. The N-bonded species were generated in dimethyl sulfoxide solvent before impregnation onto the solids, whereas the S-bonded species were generated in either *N*-methyl pyrollidone or aqueous KSCN prior to impregnation. The effect of the high surface area solid manifests itself in the reaction chemistry of copper(I) thiocyanate with 1-iodo-2-nitrobenzene (an *ipso* substitution reaction) by altering the proportion of aryl isothiocyanate to aryl thiocyanate to aryl nitrile products.

Introduction

The coordination chemistry of ligands possessing two different atoms capable of coordinating to metal ions has been a subject of interest to both the synthetic and theoretical chemist for over forty years [1–5] and the significance of this to thiocyanate was first recognised by Turco and Pecile [6] who showed that the presence of other ligands in the coordination sphere of a metal can effect the nature of the metal–thiocyanate bond.

Recently, Rannou and Chabel [7], have described the alteration of the bonding mode in copper(I) thiocyanate by changing the solvent. In DMSO for example, the copper centre preferentially binds to the nitrogen end of the thiocyanate group, whereas in solvents such as NMP of *N,N*-dimethylthioformamide (DMTF) the binding was in the expected sulfur bonded form.

Copper(I) thiocyanate is insoluble in water and in most common organic solvents, but it is readily soluble in concentrated aqueous solutions of potassium thiocyanate, which solubilises the copper(I) by forming complex species such as K[Cu(SCN)$_2$]. Copper(I) thiocyanate is also slightly soluble in dipolar aprotic solvents such as dimethyl sulfoxide (DMSO).

We have recently reported that copper(I) thiocyanate impregnated onto charcoal causes the *ipso* substitution of iodide for thiocyanate in non-polar environments [8]. This paper describes the stabilisation and characterisation of the various bonding modes of copper(I) thiocyanate on high surface area solids using diffuse reflectance Fourier transform infrared spectroscopy (d.r.i.f.t).

Experimental

The copper(I) thiocyanate was obtained from Aldrich and was purified by precipitation from a concentrated aqueous solution of potassium thiocyanate. The purification procedure was identical to that in the literature for purifying CuI [9].

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The solvents used were of AR grade or better and were distilled under reduced pressure and stored over 4A molecular sieves, prior to use.

The high surface area solids used for the work were Norit GSX (charcoal supplied by BDH Ltd.), Aerosil 200 (silica supplied by Degussa) and neutral alumina (chromatographic grade supplied by BDH Ltd.). The silica and alumina solids were dried *in vacuo* at 100 °C for 24 h prior to impregnation. The charcoal was initially dried at 300 °C for one week, and then at 100 °C *in vacuo* for 24 h prior to impregnation.

Infrared spectra were recorded on a Perkin-Elmer 1720 Fourier transform spectrometer interfaced to a dedicated Epson work station for spectral handling. Solid state spectra were run using a Specac d.r.i.f.t. accessory. The sample preparation for IR was as follows. The high surface area solid which was impregnated with copper(I) thiocyanate was finely ground with KBr using a pestle and mortar (sample: KBr 1:50). The sample was then placed in a small crucible and smoothed over with a glass plate using a circular motion to minimise any specular reflectance problems. The alumina and silica impregnated samples were scanned over the region 2300–1950 cm^{-1} requiring 10–1000 scans. The charcoal samples were scanned over the same range, but because of strong absorption by the charcoal, long term accumulations were required (typically *c.* 3000–30000 scans) and nitrogen purging.

Preparation of impregnated high surface area materials

Alumina–CuSCN (from DMSO). A 500 ml round bottomed flask was fitted with a condensor, nitrogen inlet and outlet, overhead stirrer and thermometer. To the flask was added CuSCN (1.22 g, 0.01 mol) and DMSO (200 ml), the resulting suspension was heated to 80 °C and held at this temperature until all the CuSCN had dissolved *c.* 1–2 h. Alumina (10 g) was then added and the suspension cooled to room temperature with vigorous stirring. The contents of the flask were left to stir for a further 12 h before ethoxyethane (200 ml) was added over 2 h to effect further precipitation of the salt. The impregnated solid was then filtered off at the pump washed with ethanol (3×50 ml) and ethoxyethane (3×50 ml). A free flowing light green solid was obtained which was dried at 70 °C under vacuum (<1 mm Hg) for 5 h prior to use.

Charcoal–CuSCN and silica–CuSCN were similarly prepared by impregnation from DMSO or NMP.

Impregnation from aqueous KSCN solution

Charcoal–CuSCN. To an identical set-up as above was added CuSCN (4 g, 0.03 mol) which was dissolved in aqueous KSCN (250 ml, 4 mol dm^{-3}) at 80 °C. To the resulting solution was added charcoal (10 g). The suspension was then left to cool to room temperature with stirring for 8 h. Water (30 ml/h) was added over 12 h to effect precipitation. The impregnated solid was filtered off and washed with water (5×100 ml), ethanol (5×100 ml) and ethoxyethane (5×100 ml). A free flowing powder was obtained which was dried under vacuum (<1 mm Hg) at 70 °C for 24 h prior to use.

In order not to change the solution chemistry of CuSCN by varying its concentration in solution, all concentrations were kept constant and only the amount of high surface area solid was varied.

Ipso substitution at aryl iodide

To a 100 ml round bottomed flask equipped with condenser, nitrogen inlet and outlet and overhead stirrer was added DMSO (20 ml), 1-iodo-2-nitrobenzene (1.5 g, 0.006 mol) and CuSCN (4 g, 0.03 mol). The contents of the flask were heated to 115 °C and held at this temperature for 5 h. The flask was then cooled and the contents added to water. The organic products were extracted into chloroform twice, the two organic fractions were then combined and dried over $MgSO_4$. The chloroform layer was then analysed by GC using a Carbowax 20M column. GC analysis revealed three products, 2-nitrophenyl thiocyanate, 2-nitrophenyl isothiocyanate and 2-nitrobenzonitrile, the yields were 24, 18 and 40%, respectively. Infrared analysis of the chloroform layer revealed the presence of three CN stretches at 2230 (ArCN), 2165 (ArSCN) and 2090 (ArNCS) cm^{-1}. All the other *ipso* substitution reactions listed later were similarly carried out.

Results and discussion

Impregnation of CuSCN from polar environments

Diagnostically, the best method of determining whether the copper has bonded to the sulfur or the nitrogen of the thiocyanate group is by monitoring the shift in the $\nu(CS)_{st}$ frequency. Commonly, for S-bonded species this band is in the region between 732–750 cm^{-1} and in the nitrogen bonded complexes between 792–827 cm^{-1}. For the alumina solids impregnated with CuSCN these regions are masked by structural bands belonging to the alumina, and in silica impregnated solids the bands between 792–827 cm^{-1} are masked by structural silica bands. Fortunately, several workers have used the asymmetric stretching mode of SCN to characterise the bonding present in several thiocyanate and isothiocyanate complexes [10]. Consequently, we have concentrated our efforts into looking at the 2300–1950 cm^{-1} region of the spectrum, which is also ideal because few absorptions occur here and those that do are generally weak so that $v(SCN)_{st}$ is not formally obscured.

Table 1 illustrates our results of the impregnation of copper(I) thiocyanate onto charcoal, silica and alumina high surface area solids. The $v(SCN)_{st}$ band in both thiocyanates and isothiocyanates is extremely sensitive to the mode of bonding. The most obvious difference between the various impregnated solids is the band at 2173 cm^{-1}. If we consider impregnation from aqueous KSCN we find that only charcoal stabilises the species that causes this band. The species responsible for this absorption is most likely a bridged molecule in which the sulfur of the thiocyanate group is interacting with neighbouring copper(I) centres (Fig. 1).

The proposed structure is not unreasonable, since Kabesova and coworkers have presented both IR and X-ray data to prove its existence in solid CuSCN [11, 12]. The most likely reason for the shift to higher frequency of the $v(SCN)_{st}$ level is probably due to the role of backdonating π-bonding interactions, Cu → N or Cu → S. We may visualise strong π-bond interactions from Cu → S made possible by the overlap of occupied $3d_{x^2}$ and $3d_{x^2-y^2}$ orbitals of the copper(I) centres with similar vacant π-orbitals on the sulfur of the thiocyanate group. It can be expected that π-interactions also prevail over Cu → N and consequently there is a shift in electron density from the internuclear space C–S to the space C–N.

It is interesting to note that in some cases, notably the impregnation of silica with CuSCN from aqueous KSCN and the impregnation of charcoal with CuSCN from DMSO, we may be observing hydrated and solvated species, respectively. Indeed, when the silica impregnated solid was further dried, the band at 2166 cm^{-1} decreased in intensity and in some instances disappeared, but upon hydration with water vapour the band intensity increased or reappeared. A similar phenomena was observed with the charcoal impregnated solid — here the solvated species was evident at 2169 cm^{-1}.

At loadings around 1 mmol g^{-1} of CuSCN–alumina we observe a band at 2111 cm^{-1} which is indicative of aggregate formation, i.e. $(CuNCS)_p$ (the band intensity was found to increase at higher loadings). The silica and charcoal impregnated solids only indicate signs of aggregate formation well above their monolayer capacity. Interestingly, aggregation of CuNCS on alumina appears at lower loadings *c.* 0.5 mmol g^{-1} if the impregnation solvent is NMP. Why this should be the case is not clear at this particular time, however, a solution phase spectrum of CuSCN

TABLE 1. Effect of solvent, high surface area solid and loading upon the bonding modes of copper(I) thiocyanate

Impregnated solid	Loading[a] (mmol g^{-1})	$\nu(SCN)$[b]	Assignment	Solvent[c]
CuSN		2165(s)	S-bonded	
		2173(sh,w)	bridged[d]	
Silica	1.0	2156(s)	S-bonded	aq.KSCN
		2166[e]		
		2096(w,br)	bridged[f]	
Silica	3.0[g]	2156(s)	S-bonded	aq.KSCN
		2166(sh)		
		2096(w,br)	bridged	
Alumina	1.0[h]	2156(s)	S-bonded	aq.KSCN
		2111(w)	(CuNCS)p[i]	
		2096(br)	bridged	
Charcoal	1.0	2156(s)	S-bonded	aq.KSCN
		2173(br.sh)	bridged	
Charcoal	3.3[j]	2156(s)	S-bonded	aq.KSCN
		2173(br.sh)	bridged	
Silica	3.0	2108(br)	N-bonded	DMSO
		2173(w)	bridged	DMSO
		2173(s)	bridged	DMSO
Silica	1.6	2108(br,s)	N-bonded	
Silica	0.5	2173(s)	bridged	DMSO
Silica	0.3	2173(s)	bridged	DMSO
Alumina	1.0	2165(s)	S-bonded	DMSO
		2111(br)	$(CuNCS)_p$	
Alumina	0.5	2173(s)	bridged	DMSO
		2103(br)	N-bonded	
Alumina	0.3	2173(s)	bridged	DMSO
		2103(br)	N-bonded	
Alumina	0.1	2096(br)	bridged	DMSO
Charcoal	3.3	2169[k](sh)		DMSO
		2156(w)	S-bonded	
		2107(br)	N-bonded	
		2173(s)	bridged	
Charcoal	1.0	2173(s)	bridged	DMSO
		2156(w)	S-bonded	
		2108(br)	N-bonded	
Silica	3.0	2156(s)	S-bonded	NMP
Silica	1.5	2156(s)	S-bonded	NMP
Silica	1.0	2173(w)	bridged	NMP
		2156(s)	S-bonded	
Silica	0.5	2173(w)	bridged	NMP
		2156(s)	S-bonded	
Silica	0.3	2173(w)	bridged	NMP
		2156(s)	S-bonded	
Alumina	1.0	2156(s)	S-bonded	NMP
		2111(w)	$(CuNCS)_p$	
Alumina	0.5	2156(s)	S-bonded	NMP
		2173(w)	bridged	
		2111(br)	$(CuNCS)_p$	
Alumina	0.3	2156(s)	S-bonded	NMP
		2173(s)	bridged	
Alumina	0.1	2156(s)	S-bonded	NMP
		2173(w)	bridged	
		2096(w)	bridged	
Charcoal	3.3	2156(s)	S-bonded	NMP
		2173(s)	bridged	
Charcoal	1.0	2156(s)	S-bridged	NMP
		2173(s)	bridged	

[a] Theoretical amount loaded if totally efficient precipitation. [b] Asymmetric stretching frequencies, s = sharp, w = weak, sh = shoulder, br = broad, p = aggregate CuNCS species. [c] Solvent from which impregnation took place. [d] Characteristic of a bridged species, see text. [e] Possibly a hydrated species. [f] Characteristic of a bridged species, see text. [g] Theoretical amount of material required to fill a monolayer in silica. [h] Theoretical amount of material required to fill a monolayer in alumina. [i] Aggregate CuNCS species. [j] Theoretical amount of material required to fill a monolayer in charcoal. [k] Possibly a solvated SCN species.

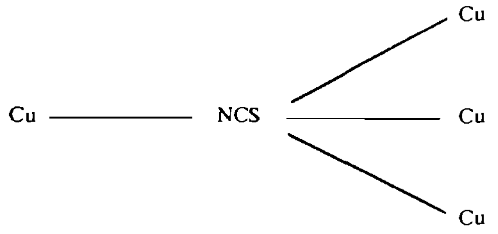

Fig. 1. Possible structure of the species stabilised by charcoal during impregnation of CuSCN from aqueous KSCN.

in NMP indicates that such species are present at *c.* 2–3%.

The major difference between DMSO and NMP impregnation is that the former predominantly stabilises N-bonded species [7], which are characterised by a broad band ($\Delta v \simeq 60$ cm^{-1}) centred at *c.* 2107 cm^{-1} compared to the sulfur bonded species which has a sharp absorption ($\Delta v \simeq 10$–15 cm^{-1}) centred at *c.* 2156 cm^{-1}. NMP impregnation shows similar behaviour to impregnation from aqueous KSCN, i.e. predominantly S-bonded species are stabilised.

The solid–'impregnation' solvent interfacial chemistry, which is inevitably taking place is most interesting. Alumina impregnation from DMSO is possibly the most fascinating. At 1 mmol g^{-1} the species stabilised by the surface is the S-bonded form (2156 cm^{-1}) together with a small contribution from the aggregate species (2111 cm^{-1}), but at 0.5 mmol g^{-1} we observe a large frequency shift and band broadening to 2103 cm^{-1} which is characteristic of the N-bonded form. Interestingly, at this loading a distinct band was observed at 2173 cm^{-1} indicating stabilisation of the tetracoordinated species mentioned above. Very little difference is observed when the loading is further reduced to 0.3 mmol g^{-1} but a relatively dramatic change occurs at 0.1 mmol g^{-1}. The band centred at 2103 cm^{-1} has been replaced by a new band at 2096 cm^{-1} which is indicative of a new di-bridged thiocyanate species (Cu–NCS–Cu). The band at 2173 cm^{-1} also disappears.

When CuSCN is impregnated onto silica from DMSO a concentration dependence pattern is again observed. At 1.5 mmol g^{-1} we observe a large broad band centred at 2108 cm^{-1} indicating an N-bonded species along with the tetracoordinated species at 2173 cm^{-1}. However, when the loading is decreased to 0.5 mmol g^{-1} only the tetracoordinated species is evident. Thus, it appears that at low loadings on silica the preferred bonding mode is the bridged species and not the N-bonded or di-bridged forms.

When considering stability it appears that at near monolayer impregnation concentrations, the alumina substrate preferentially stabilises the S-bonded thiocyanate, but at low impregnation concentrations both bridged and N-bonded thiocyanate species are stabilised by the alumina substrate.

The charcoal materials indicate very little variation with impregnation concentration. When DMSO is the solvent the dominating species is the N-bonded form. The only significant difference is the increase in intensity of the band at 2173 cm^{-1} relative to the band at 2108 cm^{-1} at near monolayer coverage (3.3 mmol g^{-1}).

The results indicate that it is possible to alter the bonding mode of copper(I) thiocyanate from the preferred S-bonded form to the N-bonded species and subsequently these modes can be stabilised by impregnation onto high surface area solids. Perhaps more significantly the work suggests that the bonding modes are affected by impregnation concentrations (relative to the amount of high surface area solid), the most dramatic case being a preferential stabilisation of the S-bonded form at high impregnation concentrations from DMSO onto alumina.

Ipso substitution of aryl iodide for thiocyanate or isothiocyanate in dipolar aprotic media

Copper(I) thiocyanate is not normally used to affect the *ipso* substitution of aryl iodide for thiocyanate or isothiocyanate, because it predominantly produces the aryl nitrile product via a base catalysed reaction in reasonable to good yields in dipolar aprotic media [13].

Nevertheless, we decided that in the light of the above observations and previous work by our group [8] it may be possible to alter the reaction chemistry of CuSCN in dipolar aprotic solvents either by addition of a high surface area solid to a conventional system or by addition of an impregnated high surface area solid, i.e. alter the ArCN:ArSCN:ArNCS ratios. Table 2 illustrates our results.

It can be seen from Table 2 that when the solvent is NMP the organic thiocyanate is the only isomer observed, presumably due to the bonding mode of the copper(I) thiocyanate in solution. When alumina is added to this system the amount of 2-nitrobenzonitrile increases compared to the experiment using an impregnated alumina. This is possibly due to a larger concentration of exposed basic sites on the alumina surface in the former case. This was shown to be plausible by addition of more solvent to dissolve off the impregnated species, thus creating more basic sites. The procedure caused an increase in the amount of aryl nitrile product.

The impregnated alumina solid when added to the DMSO system produced a ratio of 2:1 in favour of the isothiocyanate isomer although the total yield (SCN + NCS) was poor. The amount of aryl monosulfide (also caused by a base catalysed reaction)

TABLE 2. Effect of high surface area solids on the *ipso* substitution of aryl iodide in dipolar aprotic media[a]

Reagent	Support[b]	Solvent	Product	Yield (%)
CuSCN	none	DMSO	SCN[c]	24
			NCS[d]	18
			CN[e]	40
CuSCN	none	DMSO	SCN	45
			NCS	0
			CN	40
			MS[f]	15
CuSCN	alumina	DMSO	SCN	10
			NCS	12
			CN	52
CuSCN	alumina	NMP	CN	38
			SCN	52
			NCS	0
			MS	2
			DS[g]	3
CuSCN	charcoal	DMSO	SCN	25
			NCS	62
			CN	13
CuSCN	charcoal	NMP	SCN	75
			NCS	0
			CN	20
			MS	5
Alumina–CuSCN[h]		DMSO	iodobenzene	trace
			CN	33
			SCN	4
			NCS	8
			MS	50
Alumina–CuSCN		NMP	SCN	37
			NCS	30
			MS	43
			CN	20
Charcoal[i]		DMSO	CN	37
			NCS	30
			SCN	22
			MS	11
Charcoal–CuSCN[i]		NMP	CN	13
			NCS	0
			SCN	82
			MS	5

[a] Reactions carried out in the solvents noted, yields are GC yields. [b] The title support denotes addition of a high surface area solid. [c] SCN denotes thiocyanate product. [d] NCS denotes isothiocyanate product. [e] CN denotes nitrile product. [f] MS denotes aryl monosulfide. [g] DS denotes aryl disulfide. [h] Addition of impregnated alumina. [i] Addition of impregnated charcoal.

also increased. Upon addition of impregnated charcoal to the DMSO system the isomer distribution is changed to 4:3 in favour of the isothiocyanate isomer. In NMP less aryl nitrile is produced and 82% of the aryl iodide is converted into the thiocyanate isomer.

Perhaps the most important finding and certainly the most surprising is that the ratio of SCN:NCS varies only within experimental error no matter what impregnated solid is added to the dipolar aprotic media, i.e. it makes very little difference to product distribution if an impregnated charcoal solid, for example, is added to an NMP system even if that solid was impregnated from a DMSO solution. Thus it would appear that the interfacial equilibrium taking place is of utmost importance. Such equilibria must be faster than the rate of formation of either organic thiocyanate or organic isothiocyanate.

Conclusions

We have shown by the use of infrared spectroscopy that CuSCN, CuNCS and bridged thiocyanate species can be stabilised by impregnation from polar media. The stabilisation of these species is dependent upon the type of solvent, but more importantly their existence relies upon the 'impregnating' solvent–solid interfacial concentration.

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