

An NQR Study of Inclusion Compounds Formed Between Small Chlorine-containing Molecules and *bis*(N-alkylimidazolidine-2-thione)Cu(I) Halide Complexes *

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Twenty-five inclusion complexes formed by *bis*(N-alkylimidazolidine-2-thione)cuprous halides with the small, chlorine-containing guest molecules CCl₄, CHCl₃, CH₂Cl₂, CH₃CCl₃ or C₂H₄Cl₂, have been prepared. Their ⁶³Cu and ³⁵Cl NQR spectra have been measured over the temperature range 77–300 K. For the corresponding bromides the ⁷⁹Br and/or ⁸¹Br spectra have also been investigated. The studies reveal the number and symmetry of different inclusion site. The onset of rapid reorientation of the guest molecules is indicated by the fading out of their NQR signals between 77 and 300 K, whereas the resonances from the host molecules usually persist throughout this temperature range. However, as evidenced by discontinuities in the temperature-dependence of the NQR frequencies of the hosts, sixteen of the complexes show one or more phase-changes in this temperature-range.

Key words: NQR, Copper(I), Guest, Inclusion, Complex.

Introduction

We have previously demonstrated the utility of nuclear quadrupole resonance (NQR) for the study of the behaviour of small guest molecules in a variety of inclusion complexes [1–3]. The temperature-dependence of the NQR frequency depends on the temperature-variation of the mobility of the guest molecule. It would clearly be interesting to have data from quadrupolar probes in both the guest and the host molecules that would permit to correlate changes in the resonances of the guest molecules with changes in the host lattice. Our studies of the NQR spectra of ⁶³Cu and ³⁵Cl in *bis*(N-alkylimidazolidine-2-thione) cuprous halides [4, 5] revealed that they form inclusion complexes with small chlorine-containing guests, such as chloroform, when the alkyl substituent is larger than methyl: N-ethylimidazolidine-2-thione (ETIZT), N-propylimidazolidine-2-thione (PRIZT), N-isopropylimidazolidine-2-thione (iPRIZT), N-butylimidazolidine-2-thione (BUIZT), N-isobutylimidazolidine-2-thione (iBUIZT). We report here the results of

an investigation of the temperature-dependence of the ⁶³Cu and ³⁵Cl, and in some cases the ⁷⁹Br- and/or ⁸¹Br-NQR frequencies of the complexes listed in Table 1.

Table 1. The complexes studied and their numbering.

Complex	CCl ₄	CHCl ₃	CH ₂ Cl ₂	CH ₃ CCl ₃	C ₂ H ₄ Cl ₂
(ETIZT) ₂ CuCl	1	7	18	23	
(ETIZT) ₂ CuBr	2	8	19	24	
(ETIZT) ₂ CuI		9	20		
(PRIZT) ₂ CuCl	3	10			
(PRIZT) ₂ CuBr	4	11			
(PRIZT) ₂ CuI		12			
(iPRIZT) ₂ CuCl	5	13			
(iPRIZT) ₂ CuBr	6	14	21		25
(iPRIZT) ₂ CuI		15	22		
(BUIZT) ₂ CuI		16			
(iBUIZT) ₂ CuBr		17			

Experimental

a) Preparations

The host complexes were prepared as previously reported [4, 5] or by a straightforward extension of the method to another alkyl substituent. The inclusion complexes were prepared by recrystallization from the guest solvent, or for CCl₄ by recrystallisation from a 1:2 mixture of CCl₄ and (CH₃)₂CO. The complexes

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(N-methylimidazolidine-2-thione)₂CuX, (X = Cl, Br, I), (N-isopropylimidazolidine-2-thione)₂CuI and (N-butylimidazolidine-2-thione)₂CuCl did not include any of the guests. The guest CH₂Cl₂ was often lost rapidly and did not give an NQR signal. CCl₄ formed complexes only with the chlorides or bromides. Finally 1,2-dichloroethane was included only by (N-isopropylimidazolidine-2-thione)₂CuBr. Twenty-five complexes are listed in Table 1 and were characterised either by elemental C, H, N analysis or by H¹-NMR, the analytical results being shown in Table 2. A number of attempts were made to determine the crystal structure of the complexes, but difficulties arising from loss of the guest molecule and break-down of the crys-

tal prevent us from achieving any success. Any such decomposition was avoided in the NQR measurements since the samples were sealed in ampoules containing a trace of the uncomplexed guest.

b) NQR

NQR spectra were measured on a Decca super-regenerative spectrometer, frequencies being compared to harmonics from an internal crystal-controlled oscillator. Temperatures were measured with a Hewlett-Packard 2802 digital thermometer and varied between 77 K and room temperature with an Artronix 5301-E temperature controller. Although results are only reported for ⁶³Cu, ⁸¹Br and ³⁵Cl, the resonances for the isotopes ⁶⁵Cu, ⁷⁹Br and ³⁷Cl were always observed at 77 K with frequencies equal to 0.925, 1.197 and 0.788 times that of the reported isotope, respectively, thus ensuring that the resonances have been correctly attributed.

Table 2. The chemical analyses. The theoretical values are for 1:1 complexes.

Complex		%C	%H	%N
1	Found	25.51	3.97	10.87
	Theory	25.74	3.93	10.92
2	Found	23.75	3.65	9.86
	Theory	23.69	3.62	10.05
3	Found	29.10	4.55	10.35
	Theory	28.85	4.47	10.35
4	Found	26.62	4.18	9.61
	Theory	26.66	4.13	9.56
5	Found	28.80	4.43	10.24
	Theory	28.85	4.47	10.35
6	Found	26.65	4.09	9.50
	Theory	26.66	4.13	9.56
7	Found	27.33	4.27	11.61
	Theory	27.58	4.42	11.70
8	Found	25.30	3.92	10.84
	Theory	25.23	4.05	10.71
9	Found	24.02	3.93	10.51
	Theory	23.15	3.71	9.83
10	Found	31.48	5.23	11.44
	Theory	31.67	5.32	10.55
11	Found	28.07	4.48	10.08
	Theory	28.30	4.57	10.16
13	Found	30.65	4.90	11.05
	Theory	30.81	4.97	11.05
14	Found	27.92	4.55	9.99
	Theory	28.30	4.57	10.16
15	Found	25.87	4.18	9.27
	Theory	26.08	4.21	9.37
18	Found	29.57	4.89	12.60
	Theory	29.73	4.99	12.61
19	Found	26.86	4.45	11.44
	Theory	27.01	4.54	11.46
22	Found	27.62	4.60	9.96
	Theory	27.68	4.65	9.94
26	Found	30.67	4.86	11.07
	Theory	30.79	4.77	11.06

Results and Discussion

Since the spins of both copper isotopes are 3/2, the unique resonance frequency is a function of both the coupling constant and the asymmetry parameter η :

$$\nu_Q = \frac{e^2 Q q}{2} \sqrt{1 + \frac{\eta^2}{3}}.$$

For an asymmetry parameter of 0.5, the error in equating the coupling constant to twice the resonance frequency is 4%. The resonance ⁶³Cu NQR frequencies, Table 3, and, where they are available, the ⁸¹Br NQR frequencies, Table 4, of the pure complexes are all very similar to those of the inclusion complexes. The differences that do occur probably reflect small changes in the S-Cu-S bond-angle, where we have demonstrated that an increase in this angle leads to a decrease in the ⁶³Cu NQR frequency [6]. There is a rough negative correlation between the shifts of the ⁶³Cu and the ⁸¹Br resonances (Figure 1). An increase in the S-Cu-S bond-angle is expected to decrease the extent of bonding between the Cu and Br atoms [7], and if the interaction with the copper atom were the only bonding interaction undergone by the bromine atom, this would certainly lead to a decrease in the resonance frequency. For the pure host complexes *bis*(N-methylimidazolidine-2-thione)CuBr, *bis*(N-ethylimidazolidine-2-thione)CuBr and *bis*(N-

Table 3. ^{63}Cu NQR frequencies and the temperature variation of complexes **1–25**.

Complex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	Temperature	Complex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	Temperature
(ETIZT) $_2$ CuCl	30.296 30.161	30.748	−4.609	−6.480	77–RT	(PRIZT) $_2$ CuBr	28.893 29.257	29.233 29.528 28.618	−3.611 −3.440 4.773	−7.359 −1.624 −19.43	77–RT 77–191 21–312
1-CCl $_4$	29.300 29.373	29.239 29.585	3.952 −2.085	−40.82 −8.655	77–118 77–312	11-CHCl $_3$	29.219	29.477 33.176	−2.269 −29.408	−12.710 35.043	77–213 274–300
7-CHCl $_3$	30.374	30.606 23.637	−1.881 51.618	−16.663 −122.133	77–285 286–RT	(PRITZ) $_2$ CuI	27.462	27.163	−1.841	−11.44	77–RT
18-CH $_2$ Cl $_2$	30.485 30.297	30.754 30.554 29.408 30.892 28.595	−2.061 −2.094 3.214 −11.360 6.345	−16.249 −14.960 −25.720 8.410 −26.030	77–199 77–199 191–247 191–258 257–RT	12-CHCl $_3$	28.474 28.540 28.610	27.388 26.634 26.378 29.107 29.005 28.511	31.59 50.84 57.70 −7.380 −5.371 −1.802	−226.9 −338.9 −373.2 3.379 −3.766 −14.24	77–91 77–91 77–91 99–146 153–211 270–307
23-CH $_3$ CCl $_3$	29.478	29.817	−3.323	−10.59	77–300	(iPRIZT) $_2$ CuCl	32.722	33.293	−4.547	−11.164	77–RT
(ETIZT) $_2$ CuBr	29.393	29.539	−2.004	−5.737	77–RT	5-CCl $_4$	30.521 30.586 30.679	30.679 30.701 30.880	−1.573 −0.8505 −2.372	−6.858 −9.396 −3.888	77–205 77–311 77–177
2-CCl $_4$	28.414 28.484 28.568	28.815 28.844 28.964	−4.745 −4.235 −4.720	−3.180 −4.701 −3.258	77–260 77–309 77–251	13-CHCl $_3$	30.038	30.342	−3.000	−11.039	77–RT
8-CHCl $_3$	29.243	29.393	−1.337	−10.012	77–RT	(iPRIZT) $_2$ CuBr	30.343	30.953	−7.668	0.291	77–RT
19-CH $_2$ Cl $_2$	29.716 29.636	30.095 30.032 30.780 28.991 28.166 16.346	−4.247 −4.591 −14.816 9.632 −55.355 84.349	−8.287 −6.729 23.675 −63.384 −55.355 −158.752	77–138 77–138 130–167 130–167 169–273 273–RT	6-CCl $_4$	28.440 28.490 28.590	28.642 28.637 28.888	−2.150 −1.219 −3.547	−8.219 −10.91 −3.475	77–268 77–309 77–197
24-CH $_3$ CCl $_3$	28.173 28.234 28.316	28.465 28.455 28.556	−3.204 −2.016 −1.982	−6.808 −10.84 −13.75	77–143 77–308 77–120	14-CHCl $_3$	29.852 29.567	30.046 29.838	−1.697 −2.862	−12.451 −9.410	77–RT 77–RT
(ETIZT) $_2$ CuI	27.948	28.383	−5.803	0.072	77–RT	21-CH $_2$ Cl $_2$	29.141 29.210 29.308	29.474 29.515 29.549	−3.577 −3.114 −2.088	−6.940 −8.723 −12.70	77–217 77–217 ^f 77–188
9-CHCl $_3$	28.193	28.603 29.327	−4.719 −9.865	−4.377 2.520	77–225 225–300	25-C $_2$ H $_4$ Cl $_2$	29.900	30.248	−4.085	−5.251	77–RT
20-CH $_2$ Cl $_2$	28.246 28.303 28.377	28.556 28.571 28.616 31.337 30.024 3.590	−3.429 −2.611 −1.998 −23.83 −16.47 165.3	−7.917 −11.41 −14.28 27.29 17.53 −295.1	77–162 77–252 77–162 252–293 293–319 293–303	(iPRIZT) $_2$ CuI	28.591 29.042	29.097 29.325 25.352 26.707	−6.343 −2.654 24.385 12.276	−2.410 −12.450 −58.173 −36.775	77–RT 77–274 276–304 276–304
(PRIZT) $_2$ CuCl	30.046 29.295	29.939 30.706 29.688 29.633	3.770 −6.210 −4.703 −5.381	−30.457 −1.906 −2.852 0.955	77–192 232–303 77–230 232–303	15-CHCl $_3$	27.741	28.364	−7.519	4.728	77–RT
3-CCl $_4$	30.447* 30.652	30.847 30.707	−1.074 −2.481	−18.06 −7.966	77–192 221–310	22-CH $_2$ Cl $_2$	28.494	28.665	−1.106	−15.262	77–RT
10-CHCl $_3$	30.207	30.389 32.206	−0.857 −16.820	−19.301 13.161	77–213 248–300	(BuTzT) $_2$ CuI	28.448 28.548	28.765 28.880 28.382 28.349	−3.727 −4.431 1.065 −0.001	−3.955 1.888 −21.83 −16.67	77–234 77–95 97–233 233–307
						(iBuIZT) $_2$ CuBr	30.246	30.594	−4.019	−3.133	77–RT
						17-CHCl $_3$	32.310	32.714	−4.888	−4.332	77–216

* the sigmoid curve can not be fitted by a quadratic equation.

^f a sigmoid curve between 217 °K and room temperature.

isopropylimidazolidine-2-thione)CuBr the S-Cu-S angles are 123.9°, 116.2° and 112.0°, the ^{63}Cu frequencies at room temperature are 26.321, 27.756 and 28.730 MHz and the corresponding ^{81}Br frequencies are 40.87, 38.25 and 40.92 MHz, respectively [4, 6].

Table 4. ^{81}Br NQR frequencies* of complexes the **2**, **4**, **8**, **11**, **14**, **17**, **19**, **24** and **25**.

Complex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)
2	41.552	42.261 ^a	−9.952	11.560
	41.442	42.216	−9.377	0.568
4	39.83**			
8	41.636	42.112	−5.767	−3.104
11	41.524			
14	43.291			
	42.142			
17	45.322***	45.528	−1.873	−9.414
19	41.027	41.296 ^b	−2.595	−10.094
	40.392	40.428 ^b	1.403	−21.939
		42.480 ^c	−8.669	2.404
		42.211 ^c	−20.942	63.574
		40.411 ^d	15.477	65.595
		29.694 ^e	75.104	−145.399
24	40.959	41.211	−1.785	−17.800
25	42.973			

* The ^{81}Br NQR frequencies at 77 K of the pure host complexes *bis*(N-methylimidazolidine-2-thione)CuBr, *bis*(N-ethylimidazolidine-2-thione)CuBr and *bis*(N-isopropylimidazolidine-2-thione)CuBr are 41.77, 40.18 and 40.92 MHz, respectively, while that for *bis*(N-propylimidazolidine-2-thione)CuBr was only observed at 40.91 MHz at room-temperature, [4].

** At room temperature; *** ^{79}Br resonance.

^a 77–110 K; ^b 77–136 K; ^c 130–166 K

^d 169–248 K; ^e 283–304 K.

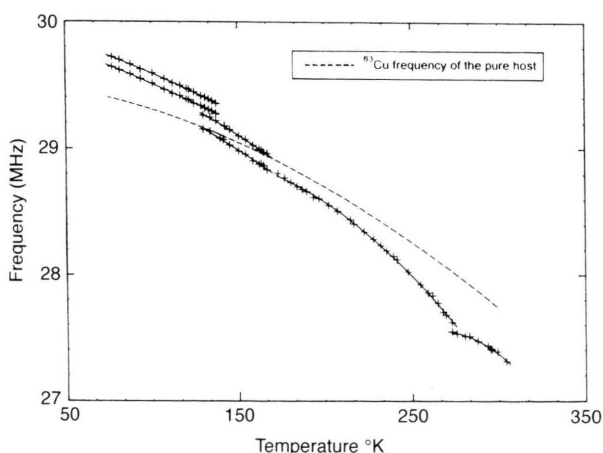


Fig. 1. ^{63}Cu NQR frequencies of $(\text{ETIZT})_2\text{CuBr} \cdot \text{CH}_2\text{Cl}_2$ (**19**).

Although the ^{63}Cu frequencies correlate well with the bond-angle, the correlation with the ^{81}Br resonance frequency is not well defined. The crystal structures of the imidazolidine-2-thione complexes clearly indicate significant hydrogen-bonding between the bromine atom and the hydrogen atoms on the two adjacent NH groups of the imidazolidine ring [6], and a decrease in the Cu-Br bond-length will modify the Br-H interaction both with respect to the degree of bonding and to the H-Br-H angle. The net results of these modifications on the ^{81}Br frequencies are thus difficult to predict.

As revealed by the temperature-dependence of their ^{63}Cu NQR spectra and of their ^{81}Br spectra, sixteen of the twenty-five complexes studied, **2–4**, **7**, **9–12**, **15–21**, and **25**, showed phase changes in the range 77–300 K. The temperature-dependence of each phase of each complex was fitted to a quadratic equation

$$\nu_T = \nu_0 + AT + BT^2.$$

The parameters of these quadratics, together with the frequencies observed at 77 K and temperature ranges are shown in Tables 3 and 4 for the ^{63}Cu and ^{81}Br nuclei, while Tables 5a–5e show the ^{35}Cl reso-

Table 5a. ^{35}Cl NQR frequencies of CCl_4 guest molecules. f_T is the fade out temperature.

Complex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	f_T (K)
1	40.281	40.713	−5.099	−6.155	164.5
	40.193	40.633	−5.307	−5.465	143.5
2	40.728	39.900	23.34	−163.9	110.7
	40.711	40.339	13.82	−117.0	110.7
	40.357	40.388	2.922	−42.5	102.7
	40.289	40.002	9.149	−70.05	102.7
		40.160	4.072	−35.93	141
3	41.009	40.907	6.334	−64.47	110.7
	40.730	40.253	14.45	−107.5	116.7
	40.282	40.466	0.252	−33.05	123.3
	40.282	40.580	0.164	−50.74	110.7
	40.124	40.412	1.921	−73.39	111.8
4	40.52*				
	40.15*				
5	40.762	41.028	−2.137	−17.00	140.4
	40.609	41.026	−4.400	−11.95	140.4
	40.503	40.849	−3.361	−10.74	175.5
	40.300	40.577	−0.456	−38.50	140.4
6	40.959	41.092	−0.813	−12.15	149.5
	40.636	40.872	−2.337	−8.471	139.5
	40.559	40.652	−0.182	−15.10	154.0
	40.541	40.010	−6.170	4.335	154.0

* Frequencies at 100 K.

Table 5b. ^{35}Cl NQR frequencies of CHCl_3 guest molecules. f_T is the fade out temperature.

Com- plex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	f_T (K)
7	38.183	38.728	−6.300	−10.350	167
7	37.658	38.139	−4.514	−15.926	
7	37.581	37.866	−2.029	−20.372	
8	38.336	39.103	−8.675	−14.334	112
8	37.560	38.067	−5.211	−17.028	
8	37.436	37.951	−3.463	−40.189	
9	38.217	38.449	−2.045	−11.507	219
9	37.978	38.443	−5.872	0.215	
9	37.777	37.961	−0.553	−24.762	
9		39.112	−6.920	0.566	
9		38.778	−5.932	2.544	
9		38.653	−6.984	2.718	
10	38.113	38.511	−3.738	−17.771	143
10	37.703	38.236	−5.713	−14.617	
10	37.363	37.884	−6.102	−8.188	
11	38.074	38.528	−4.500	−16.814	143
11	37.662	38.198	−5.373	−18.931	
11	37.379	37.881	−5.367	−13.952	
12	38.310	38.681	−4.590	−2.139	121
12	37.901	38.190	−0.767	−37.71	125
12	37.495	38.106	−4.889	−23.32	125
13	37.910	38.135	−5.313	−106.800	107
13	37.671	38.413	−7.821	−22.748	
13	37.400	38.039	−2.656	−72.359	
14	38.256	38.612	−2.581	−26.976	158
14	38.001	38.416	−3.323	−26.244	
14	37.945	38.339	−4.329	−8.679	
14	37.879	38.146	−2.432	−12.681	
14	37.749	38.017	−1.270	−28.003	
14	37.700	37.956	−0.776	−33.133	
15	38.197	38.544	−2.972	−21.049	
15	38.083	38.345	−1.645	−22.236	
15	37.798	38.270	−5.470	−8.050	
16	38.585	38.841	−1.629	−21.36	143
16	38.266	38.432	−0.593	21.12	172
16	38.109	38.605	−5.195	−14.25	145
16	37.812	38.090	−1.888	−22.27	145
16	37.812	38.460	−8.008	−3.449	145
16	37.642	38.071	−3.854	−20.09	145
17	38.091	38.372	−3.088	−7.097	171
17	37.948	38.413	−5.277	−9.122	179
17	37.816	38.441	−7.428	−7.704	169

Table 5c. ^{35}Cl NQR frequencies of CH_2Cl_2 guest molecules. f_T is the fade out temperature.

Com- plex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	f_T (K)
18	35.857	35.203	19.964	−151.620	116
	35.784	35.784	6.602	−85.705	140
	35.654	35.883	−0.309	−34.568	153
	35.505	35.592	2.313	−44.592	166
19	35.999	36.581	−7.230	−3.019	113
	35.864	37.019	−19.300	58.568	
	35.581	36.633	−17.140	46.977	
	35.512	36.241	−10.240	−11.818	
20	36.047	36.334	−1.940	−24.33	215
	36.009	36.083	1.266	−30.13	
21	36.345	36.250	4.777	−48.66	178
	36.124	36.223	1.373	−35.67	
22	36.175	36.276	1.729	−40.112	171
	36.112	36.273	0.770	−38.007	

Table 5d. ^{35}Cl NQR frequencies of CH_3CCl_3 guest molecules. f_T is the fade out temperature.

Com- plex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	f_T (K)
23	38.295	38.408	0.0721	−19.84	162
	38.026	38.133	−0.260	−14.46	162
	37.885	38.112	−2.746	−1.631	167
24	38.239	38.111	5.069	−45.75	151
	38.006	37.879	4.719	−40.83	151
	37.841	37.962	−0.684	−11.55	162

Table 5e. ^{35}Cl NQR frequencies of $\text{C}_2\text{H}_4\text{Cl}_2$ guest molecules. f_T is the fade out temperature.

Com- plex	ν_{77} (MHz)	ν_0 (MHz)	A (kHz K $^{-1}$)	B (Hz K $^{-2}$)	f_T (K)
25	34.680(7)	34.333	8.486	−54.836	261

nances of the guest molecules CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3CCl_3 and $\text{C}_2\text{H}_2\text{Cl}_2$, respectively. The last columns of these Tables also show the fade-out temperature of the resonances of the guest molecules. Not all the temperature-dependences can be fitted to a quadratic, for example **3** and **21** have sigmoid curves. Finally Table 6 lists the temperatures at which phase-changes occur.

A particularly rich example of multiple phases is furnished by **19**, where both nuclei of the host molecule have been observed. Figures 2 and 3 show respec-

tively the temperature-dependence of the ^{63}Cu and ^{81}Br resonances. There are two low-temperature phases with two distinct host-molecules in the unit cell and two phases at higher temperatures with only one distinct host-molecule. The ^{35}Cl spectrum consists of two closely-spaced pairs of lines only in the lowest temperature phase (fade-out at 113 K), indicative of the presence of two distinct guest CH_2Cl_2 molecules, both of which are in an asymmetric site. A first-order phase-change occurs at around 130 K, but with slow warming or cooling it is possible to observe the coex-

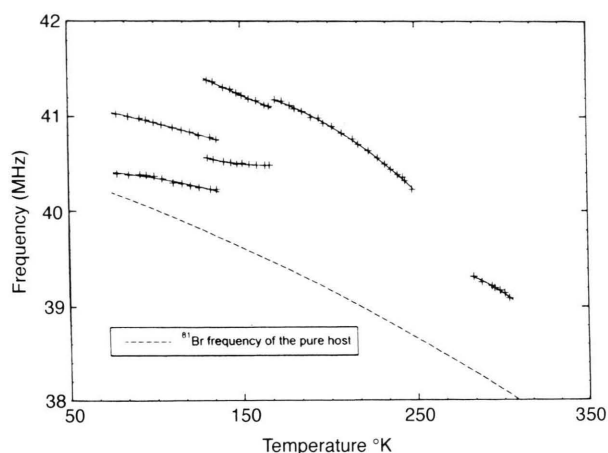


Fig. 2. ^{81}Br NQR frequencies of $(\text{ETIZT})_2\text{CuBr} \cdot \text{CH}_2\text{Cl}_2$ (19).

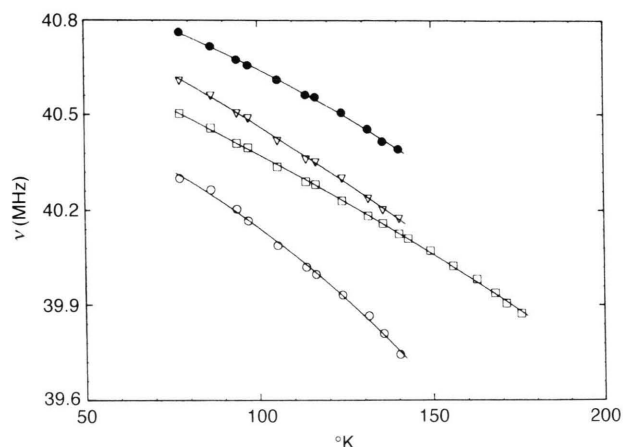


Fig. 3. ^{35}Cl NQR frequencies of $(\text{iPRIZT})_2\text{CuCl} \cdot \text{CCl}_4$ (5).

istence of the two phases and the consequent overlapping of both the ^{63}Cu and the ^{81}Br spectra in the range 130–140 K. At 169 K a further transition occurs and the two resonances for each nucleus collapse to a single line. Whereas the ^{81}Br resonance slowly fades out as the temperature increased, the ^{63}Cu line persists up to 272 K, where a further phase-change occurs and the ^{81}Br resonance appears. Also shown in the Figures is the temperature-dependence of the corresponding frequencies for the pure host complex. The general similarity between both the resonance frequencies and the temperature dependence of these frequencies for the inclusion complex and the empty host shows that the formation of the inclusion complex

Table 6. Phase transition temperatures in complexes **2–4**, **7**, **9–12**, **15–21**, **25**.

Complex	Nucleus	Transition temperature (K)
2	^{35}Cl	110.5
3	^{63}Cu	192–221
4	^{63}Cu	191–212
7	^{63}Cu	285
9	^{63}Cu	225
	^{35}Cl	163–165
10	^{63}Cu	213–248
11	^{63}Cu	213–274
12	^{63}Cu	91–99
		146–153
		211–270
15	^{63}Cu	274–276
16	^{63}Cu	95–97
		233
17	^{63}Cu	216
	^{79}Br	217
18	^{63}Cu	191–199
		257–258
19	^{63}Cu	130–138
		169
		273
19	^{81}Br	130–136
		169
		248–283
20	^{63}Cu	252
		293
21	^{63}Cu	217
25	^{35}Cl	—

does not bring about any major alteration of the structure of the copper complex.

The number of NQR signals given by a particular host is an indication of the symmetry of the inclusion site. For CCl_4 three types of behaviour were observed; for **1** and **4** only two signals with the same intensity could be seen, indicative of a site of C_{2v} symmetry, while complexes **2**, **5** and **6** showed four signals and, although it is possible that this could be due to two different sites of C_{2v} symmetry, the more economical interpretation is that the sites are essentially bereft of any significant symmetry element. Finally, **3** exhibits a more complex pattern of signals. Five resonance lines are visible at 41.009, 40.730, 40.282, 40.282 and 40.124 MHz with an intensity ratio of 1:3:1:2:1. Two of them are noticeable more intense than the others. A possible explanation of this is that there is one site of C_{3v} symmetry, giving two signals with intensity ratio of 1:3, and one site where there is only a mirror plane

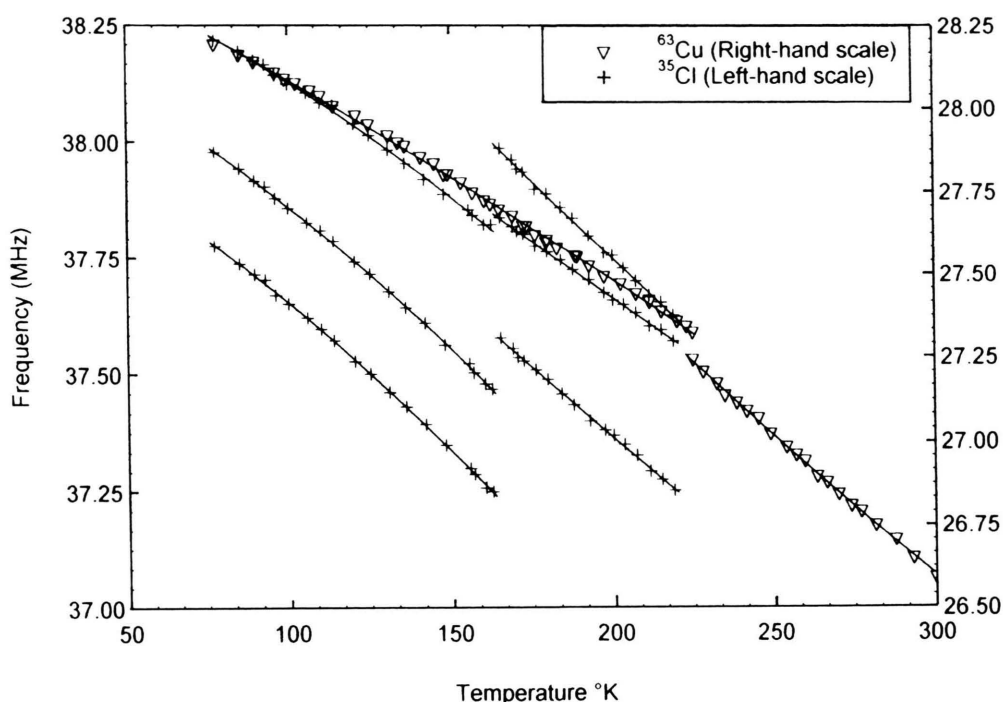


Fig. 4. ^{35}Cl and ^{63}Cu NQR frequencies of $(\text{ETIZT})_2\text{CuI} \cdot \text{CHCl}_3$ (**9**).

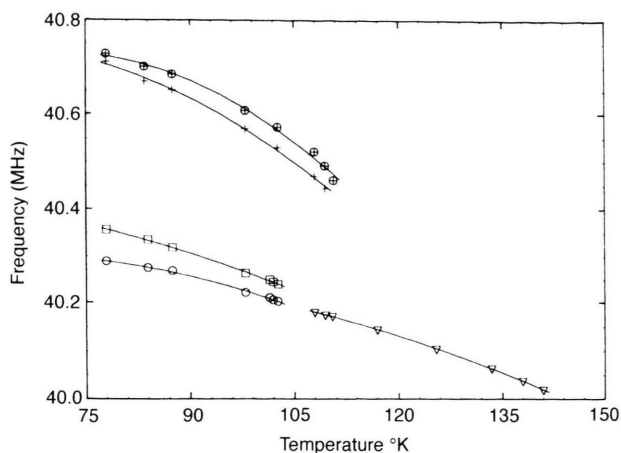
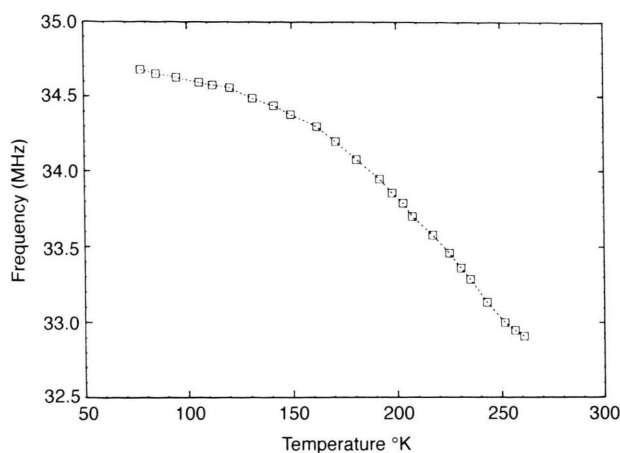
so that there are three signals in an intensity ratio of 2:1:1.

Guest molecules of CHCl_3 give rise to three signals in almost every case (**7–13**, **15**, **17**), again indicating that the guest is at a site of low symmetry. Complexes **14** and **16** gave six resonances, so that for these complexes there are at least two sites, both of low symmetry. CH_2Cl_2 shows a similar behaviour, where **20**, **21** and **22** show the two signals characteristic of inclusion sites of low symmetry while **18** and **19** show four resonances indicating that for these complexes there are at least two distinct inclusion sites.

In most cases the ^{35}Cl resonances of the guest molecule were visible only at low temperatures, usually fading out at temperatures in the range 100–200 K. As discussed in [1–3], this behaviour is due to the fact that the guest molecule can reorient within the cavity or channel of the host crystal and that, when this molecular reorientation is sufficiently rapid, the ^{35}Cl line broadens and disappears. In several cases one of the lines persists to higher temperature than the others. An example of this is shown in Fig. 4 for complex **5**, where three of the four lines of the CCl_4 guest fades out at around 140 K while the remaining line persists

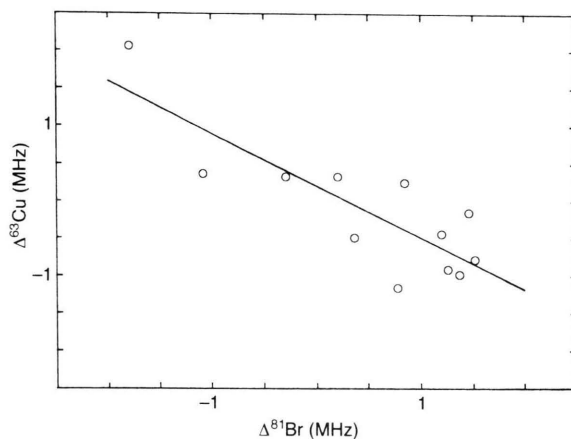
up to 175 K. This behaviour is reminiscent of the behaviour of CCl_4 included in cavities with three-fold symmetry [1–3] with one of the CCl bonds – the axial chlorine atom – lying along the three-fold axis, where there are therefore only two resonances with intensity-ratios 3:1. The site symmetry permits easy rotation about the three-fold symmetry axis so that the more intense lines – arising from the three equatorial chlorine atoms – fade out rapidly, but since rotation about the three-fold axis does not alter the direction of the field-gradient z axis of the axial chlorine atom its resonance remains visible until a more general tumbling motion sets in. The cavity in **5** is thus probably elongated but of low symmetry, so that the three equatorial chlorine atoms are not absolutely equivalent.

In two cases a discontinuity of the resonances of the guest molecule is not reflected in the resonances of the host lattice; they must be associated with second-order phase changes that involve motion of only the guest molecule. The results for **9** are shown in Figure 5. For this complex the ^{63}Cu signal shows that the host molecules occupy just one crystallographically-equivalent site while the three resonances of the guest molecule show that the inclusion site is bereft of sym-

Fig. 5. ^{35}Cl NQR frequencies of $(\text{ETIZT})_2\text{CuBr} \cdot \text{CCl}_4$ (**2**).Fig. 6. ^{35}Cl NQR frequencies of $(\text{iPRIZT})_2\text{CuBr} \cdot \text{C}_2\text{H}_4\text{Cl}_2$ (**25**).

metry. The change in the ^{35}Cl resonances at 167 K is not accompanied by the slightest discontinuity in the ^{63}Cu signals, indicating that the only change is in the nature of the inclusion site. The signals in the second low temperature phase persist up to 220 K, just a few degrees below the temperature where the ^{63}Cu signal shows a discontinuity that is evidence of yet another phase-change. The persistence of the resonances of the guest molecule up to this rather high temperature is an indication either that the volume of the inclusion cavity in the temperature range 77–220 K is lower or that the host-guest interactions are greater than those for the high-temperature phase.

Another example of a discontinuity occurring only for the guest molecule is shown for **2** in Figure 5. From 77 K to 110 K the resonances of CCl_4 are two closely-spaced doublets, but above this temperature the higher frequency pair disappears while the lower frequency pair collapses to a single line with an increased intensity. The fact that all four lines disappear at the almost same temperature implies that the four signals are due to four inequivalent chlorine atoms of CCl_4 occupying just one inclusion site but, in the absence of a crystal-structure determination, we cannot exclude the possibility that they arise from two different sites, each having C_{2v} symmetry. The single line that persists after the phase-change implies, as for **5**, a motion of the guest molecule that considerably alters the directions of the field-gradient tensors for the high-frequency pair while provoking only a small variation in the directions of the tensors of the low-frequency pair.

Fig. 7. The correlation of $\Delta^{81}\text{Br}$ and $\Delta^{63}\text{Cu}$ between clathrates and pure complexes.

The absence of any discontinuity in the resonance of the host lattice militates against the alternative explanation that the CCl_4 guest now occupies a site with T_d symmetry.

In view of the bulk of the guest molecule it is not surprising that, apart from **9**, the only complex for which the ^{35}Cl resonance of the guest molecule persists up to relatively high temperatures is **25**. Only one resonance is observed, thus showing that the site of the guest molecule has at least one element of two-fold symmetry so that the equivalence of the two chlorine atoms is preserved. More interesting is the shape of the temperature dependence (Figure 7). From 77 K to

177 K the frequency drops by 0.6 MHz, but by the time the resonance fades out some 80 K later the frequency has dropped by a further 1.3 MHz while just before the fade-out the temperature dependence has flattened out somewhat. This behaviour recalls that of the pure crystalline guest molecule where the ^{35}Cl temperature-dependence has a sigmoid shape that has been shown to arise from the onset of rapid rotation about an axis going approximately through the line joining the two chlorine atoms [8]. The rapid rotation of a molecule about an axis having an angle θ with respect to the field-gradient z -axis reduces the resonance frequency according to the equation

$$\frac{\nu_{\text{rotating}}}{\nu_{\text{static}}} = \frac{3 \cos^2 \theta - 1}{2}.$$

In *trans*-dichloroethane the line joining the two chlorine atoms has an angle of 19° to the C-Cl bonds, and thus to the principal axis of the ^{35}Cl field-gradient, so that rapid rotation reduces the coupling constant by the factor 0.84. We have not, however, succeeded in observing the ^{35}Cl signal at temperatures up to 300 K where, if our hypothesis is correct, we might have expected to observe the resonance once again. However, if other types of reorientation are also facil-

itated at this relatively high temperature, the ^{35}Cl signal would no longer be visible.

Conclusion

We have used ^{63}Cu , ^{35}Cl and ^{81}Br NQR to study a new series of inclusion compounds formed by *bis*(*N*-alkylimidazolidine-2-thione)cuprous halides with small chlorine-containing guest molecules, such as CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3CCl_3 and $\text{C}_2\text{H}_2\text{Cl}_2$. When both host and guest resonances can be studied, NQR is a particularly appropriate method for the study of inclusion compounds, especially for unstable compounds since we may leave them in contact with the pure guest. The site multiplicity and the site symmetry of the guests are indicated by the number of their resonance lines, while the temperature dependence curves reveal the phase changes and motions of the guest molecule.

Acknowledgements

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- [1] L. Pang, E. A. C. Lucken, and G. Bernardinelli, *J. Amer. Chem. Soc.* **112**, 221 (1989).
- [2] L. Pang, E. A. C. Lucken, J. Weber, and G. Bernardinelli, *J. Comput. Aided Mol. Des.* 285 (1991).
- [3] L. Pang, E. A. C. Lucken, and G. Bernardinelli, *J. Inc. Phenomena and Mol. Rec. in Chem.* **13**, 63 (1992).
- [4] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, *Z. Naturforsch.* **47a**, 125 (1992).
- [5] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, *J. Chem. Soc. Dalton Trans.* 1185 (1993).
- [6] S. Ramaprabhu, E. A. C. Lucken, and G. Bernardinelli, *J. Chem. Soc. Dalton Trans.* 113 (1995).
- [7] J. F. Riehl, El-Idrissi Rachidi, Y. Jean, and M. Pelissier, *New J. Chem.* **15**, 239 (1991).
- [8] J. L. Ragle, *J. Phys. Chem.* **63**, 1395 (1967).