Crystal Structure and NQR of Two Copper(I) Complexes of 4,6-Dimethylpyrimidine-2-thione *

Sundara Ramaprabhu and Edwin A. C. Lucken
Département de Chimie Physique, Université de Genève, 30, quai Ernest-Ansermet,
1211 Genève 4, Switzerland

Gérald Bernardinelli
Laboratoire de Cristallographie, Université de Genève, 24 quai Ernest-Ansermet,
1211 Genève 4, Switzerland

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The crystal structure and ^{63}Cu NQR spectra of two neutral hexanuclear Cu(I) complexes of 4,6-dimethylpyrimidine-2-thione, (Hdmpt); $[dmptCu]_6 6CHCl_3$ (**1**) and $[dmptCu]_6C_2H_4Cl_2$ (**2**), are reported. The number and relative intensities of the NQR resonances are in agreement with the results of the crystallographic study. The temperature-dependence of the resonances reveals that both compounds undergo a phase-change in the temperature range 77 K – 300 K, both of which may be associated with the loss of a symmetry-element present in the high-temperature phase. The ^{35}Cl resonances of $CHCl_3$ in **1** could be observed in the low-temperature phase but the corresponding resonances for $C_2H_4Cl_2$ in **2** were not detected.

Key words: ^{63}Cu; ^{35}Cl; Cu(I); Crystal structure.

Introduction

The recent publication of the structure of a complex formed between 4,6-dimethylpyrimidine-2-thione and Copper(I), $[Cu_6(dmpt)_6] \cdot H_2O$, [1], prompts us to report the results of a crystallographic and NQR study of two closely-related complexes, **1**, $[Cu(dmpt)]_6 \cdot 6CHCl_3$ and **2**, $[Cu(dmpt)]_6 \cdot C_2H_4Cl_2$, that were prepared in the course of an extensive investigation of the ^{63}Cu NQR spectra of a variety of Cu(I) complexes [2–7].

Experimental

Preparation

$[Cu(dmpt)]_6 \cdot 6CHCl_3$, **1**, and $[Cu(dmpt)]_6 \cdot C_2H_4Cl_2$, **2**, were prepared by dissolving Cu_2O (0.72 g, 0.005 mol) in a solution of 4,6-dimethylpyrimidine-2-thione (2.8 g, 0.02 mol) in either chloroform, **1** or 1,2-dichloroethane, **2**, and evaporating the yellow-orange solution [8]. An analogous preparation using dichloromethane as a solvent gave a yellow-orange product, **3**, for which we were unable to observe either ^{63}Cu or ^{35}Cl NQR signals. All three complexes gave reasonably satisfactory analyses. **1** C 27.73%, H 2.79%, N 9.44% (Theory 26.10, 2.50, 8.70); **2** C 34.56%, H 3.64%, N 12.79% (Theory 34.70, 3.52, 12.78), **3** C 34.71%, H 3.68%, N 13.48% (Theory for $[Cu(dmpt)]_6 \cdot CH_2Cl_2$; 35.07, 3.41, 12.92, theory for [Cu(dmpt)]; 35.54, 3.48, 13.82). The discrepancies between the theoretical and experimental analyses for **1** are undoubtedly due to the ease with which it loses the included solvent molecules. The microanalyses were carried out by Dr. H. Eder of the University of Geneva Micro analytical Laboratory.

X-ray Crystallography

Single crystals of **1** and **2** were obtained by slow evaporation from $CHCl_3$ and $C_2H_4Cl_2$ solutions, respectively. The crystals of **1** were mounted in Lindemann capillaries with the solvent of crystallization to prevent degradation. The cell parameters and diffracted intensities were measured at room temperature on a Philips PW1100 and a Nonius CAD4 diffractometers with graphite-monochromated Mo[Kα] radiation ($\lambda = 0.71069$ Å). Two reference reflections

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Reprint requests to Prof. Dr. E. A. C. Lucken, Dept. of Physical Chemistry University of Geneva, 30 Quai Ernest-Ansermet, 1211 Geneva 4, Switzerland.

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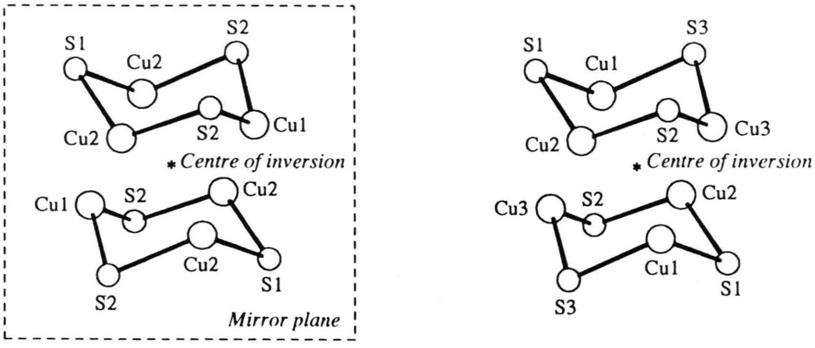


1 **2**

Fig. 1. Perspective view of the six-membered rings showing the equivalence of the atomic sites of **1** (a) and **2** (b)

Table 1. Summary of crystal data, intensity measurement and structure refinement of compounds **1** and **2**.

Formula	**1**[a]	**2**[b]
Mol. wt.	1932.7	1315.4
Crystal system	Monoclinic	Triclinic
Space Group	C2/m	$P\bar{1}$
a (Å)	19.400(2)	11.527(4)
b (Å)	18.509(3)	11.673(4)
c (Å)	10.609(2)	11.844(5)
α (°)	90	84.53(2)
β (°)	98.16 (1)	73.53(2)
γ (°)	90	65.82(2)
V (Å^3)	3771 (1)	1393.8(8)
Z	2	1
F (000)	1920	662
Dc gr.cm^{-3}	1.70	1.57
μ (Mo Kα) mm^{-1}	2.511	2.607
A^* min., max.	1.910, 2.284	1.295, 1.512
$((\sin\theta)/\lambda)_{\max}$ (Å^{-1})	0.60	0.58
Temperature (K)	298	298
No. measured reflc.	3693	4376
No. observed reflc.	2335	3658
Criterion for observed	$\lvert Fo\rvert > 4\sigma(Fo)$	$\lvert Fo\rvert > 4\sigma(Fo)$
Refinement (on F)	Full-matrix	Full-matrix
No. parameters	208	297
Weighting scheme	$\omega = 1/\sigma^2(Fo)$	$\omega = 1$
Max. and average Δ/σ	0.017, 0.002	0.54, 0.006
Max. and min. $\Delta\varrho$ (e.Å^{-3})	1.23, −1.58	1.42, −0.78
S	5.13	2.15
R, ωR	0.072, 0.056	0.061, 0.061

[a] $[Cu(C_6H_7N_2S)]_6(CHCl_3)_6$
[b] $[Cu(C_6H_7N_2S)]_6(C_2H_4Cl_2)$

measured every 60 minutes showed an increase of about 16% of the diffracted intensities for **1** (all intensities were corrected for this drift) and variations less than 3.5σ (I) for **2**. Data were corrected for Lorentz and polarization effects and for absorption [9]. The structures were solved by direct methods using MULTAN 87 [10], all other calculations used XTAL [11] system and ORTEP [12] programs. Atomic scattering factors and anomalous dispersion terms were taken from [13]. All coordinates of the hydrogen atoms were calculated. A summary of crystal data, intensity measurement and structure refinement in Table 1. Final coordinates and selected geometrical parameters are reported in Tables 2 and 3, respectively. Figure 1 shows a perspective view of the six-membered rings showing the equivalent atomic sites for **1** and **2** while Fig. 2 is a stereoscopic drawing of **1**, initial in all essential respects to that of **2**. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW, England.

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.

Results

X-Ray Crystallography

Complexes **1** and **2** both contain copper atoms with an essentially trigonal-planar $CuNS_2$ coordination. Both complexes are formed of 6 CuL units (L=4,6-dimethylpyrimidine-2-thione) related by a center of inversion. Moreover in **1**, two CuL are located in special position in a mirror plane (Wyckoff site 4i). The

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) with e.s.d.'s in parenthesis. U_{eq} is the average of eigenvalues of U.

	x/a	y/b	z/c	U_{eq}
Compound **1**				
Cu(1)	0.03429(8)	1/2	0.2084(1)	0.062(1)
Cu(2)	0.07661(6)	0.58197(8)	0.01550(9)	0.0649(8)
S(1)	0.1608(2)	1/2	0.0584(3)	0.065(2)
N(1)	0.1325(5)	1/2	0.2972(9)	0.057(7)
N(2)	0.2521(6)	1/2	0.2637(9)	0.063(8)
C(1)	0.1853(7)	1/2	0.225(1)	0.056(9)
C(2)	0.1525(7)	1/2	0.424(1)	0.06(1)
C(3)	0.2211(7)	1/2	0.473(1)	0.07(1)
C(4)	0.2710(7)	1/2	0.389(1)	0.07(1)
C(5)	0.0933(8)	1/2	0.500(1)	0.10(1)
C(6)	0.3466(8)	1/2	0.432(1)	0.08(1)
S(11)	−0.0361(1)	0.5975(1)	0.1934(2)	0.056(1)
N(11)	0.0685(4)	0.6725(5)	0.1192(6)	0.057(5)
N(12)	−0.0048(4)	0.7345(5)	0.2475(7)	0.060(5)
C(11)	0.0134(4)	0.6756(6)	0.1865(8)	0.053(6)
C(12)	0.1054(5)	0.7313(7)	0.1151(9)	0.068(7)
C(13)	0.0915(5)	0.7945(6)	0.176(1)	0.075(7)
C(14)	0.0346(5)	0.7933(6)	0.2432(8)	0.066(7)
C(15)	0.1653(5)	0.7280(7)	0.038(1)	0.096(8)
C(16)	0.0153(6)	0.8577(7)	0.319(1)	0.108(9)
C(01)	0.1622(8)	0	−0.017(2)	0.09(1)
Cl(1)	0.1779(3)	0	0.1486(5)	0.145(4)
Cl(2)	0.1183(4)	0.0720(3)	−0.0678(4)	0.318(7)
C(02)	0.8438(5)	0.2849(7)	0.355(1)	0.088(8)
Cl(01)	0.7822(2)	0.3465(2)	0.2910(3)	0.116(3)
Cl(02)	0.8154(2)	0.1975(2)	0.3245(4)	0.155(4)
Cl(03)	0.8627(2)	0.3001(3)	0.5192(3)	0.188(4)
Compound **2**				
Cu(1)	0.6848(1)	0.4645(1)	0.5343(1)	0.0482(5)
Cu(2)	0.5682(1)	0.4604(1)	0.3178(1)	0.0482(5)
Cu(3)	0.4950(1)	0.3240(1)	0.54054(9)	0.0470(5)
S(1)	0.7632(2)	0.4487(2)	0.3376(2)	0.0435(9)
S(2)	0.5331(2)	0.2842(2)	0.3496(2)	0.0430(9)
S(3)	0.6741(2)	0.2832(2)	0.6064(2)	0.0433(9)
N(11)	0.6539(7)	0.6994(7)	0.3335(6)	0.047(3)
N(12)	0.8565(8)	0.5935(8)	0.1885(7)	0.058(4)
C(11)	0.7578(8)	0.5949(8)	0.2820(7)	0.044(4)
C(12)	0.651(1)	0.8101(9)	0.2880(9)	0.058(5)
C(13)	0.750(1)	0.815(1)	0.192(1)	0.071(6)
C(14)	0.851(1)	0.707(1)	0.146(1)	0.068(5)
Cl(15)	0.533(1)	0.924(1)	0.348(1)	0.094(7)
C(16)	0.967(1)	0.703(1)	0.045(1)	0.103(8)
N(21)	0.2798(7)	0.4298(7)	0.3653(6)	0.044(3)
N(22)	0.3713(8)	0.2289(7)	0.2702(7)	0.057(4)
C(21)	0.3789(8)	0.3175(8)	0.3271(7)	0.041(4)
C(22)	0.164(1)	0.458(1)	0.3400(9)	0.058(5)
C(23)	0.148(1)	0.373(1)	0.280(1)	0.070(6)
C(24)	0.253(1)	0.258(1)	0.248(1)	0.069(6)
C(25)	0.060(1)	0.585(1)	0.378(1)	0.075(6)
C(26)	0.245(2)	0.158(1)	0.182(1)	0.111(9)
N(31)	0.4977(7)	0.4082(7)	0.8004(6)	0.046(3)
N(32)	0.6649(9)	0.2105(7)	0.8253(7)	0.065(4)
C(31)	0.6063(9)	0.3019(8)	0.7593(7)	0.046(4)
C(32)	0.438(1)	0.418(1)	0.9165(8)	0.058(5)
C(33)	0.495(1)	0.324(1)	0.9898(9)	0.076(6)
C(34)	0.605(1)	0.223(1)	0.944(1)	0.082(7)
C(35)	0.315(1)	0.530(1)	0.961(1)	0.077(6)
C(36)	0.678(2)	0.122(1)	1.106(1)	0.14(1)
Cl(1)	0.0538(7)	−0.0613(9)	0.8220(6)	0.115(5)*
Cl(2)	0.144(1)	0.1026(7)	0.5080(8)	0.149(5)*
C(01)	0.132(5)	0.022(5)	0.597(5)	0.20(2)*
C(02)	0.023(6)	0.028(5)	0.683(5)	0.21(2)*

[a] Atomic sites refined with a population parameter of 0.5.

Table 3. Mean values of bond lengths (Å) and bond angles (°)

Cu–S(intra-annular)	2.25(2)	Cu–S–Cu	90(4)
Cu ··· S(inter-annular)	3.11(2)	S–Cu–S	113(5)
Cu–N	2.02(1)	S–Cu–N	119(6)
S–C	1.75(1)	Cu–S–C	106(4)

structure of the complex is similar to (CuL)$_6$/H$_2$O [1] and can be described as two six-membered rings formed by an alternated of Cu and S atoms bridged by six 4,6-dimethylpyrimidines. The six-membered rings adopt a quasi-perfect chair conformation with intra-annular torsion angles in the range 70.5 to 80.4°. The two six-membered rings of one complex are stacked around a center of inversion, and the copper and sulphur atoms form two staggered octahedrons.

Both compounds include solvent molecules in a ratio of 1:6 and 1:1 for **1** and **2**, respectively. In the compound **1**, the CHCl$_3$ molecules are ordered but show significant values of atomic displacement parameters; one of them is located in general position and the other on a mirror plane (4i). In **2**, the atomic sites of the C$_2$H$_4$Cl$_2$ molecule have been refined with a population parameter of 0.5. The pyrimidine rings show no distortion from planarity.

NQR

The ^{63}Cu NQR frequencies were observed in the range 77–302 K, and the results are shown graphically in Figs. 3 and 4. Whereas at room-temperature the number of distinct ^{63}Cu resonances corresponds to the number of inequivalent Cu sites revealed by the room-temperature structure determination of the complexes, at a lower temperature a phase-change occurs that results, in both cases, in an increase in the number of resonances. The temperature dependence

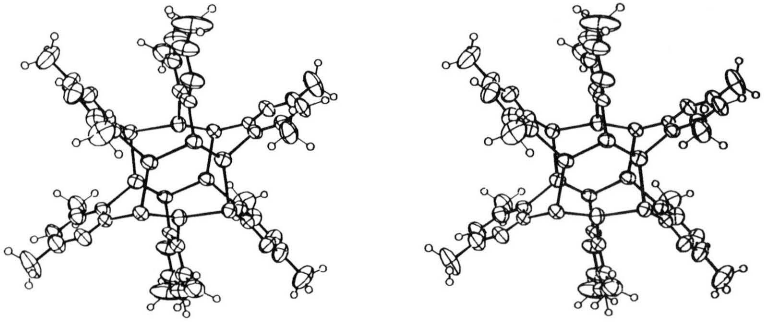


Fig. 2. Stereoscopic projection of the structure of **1**.

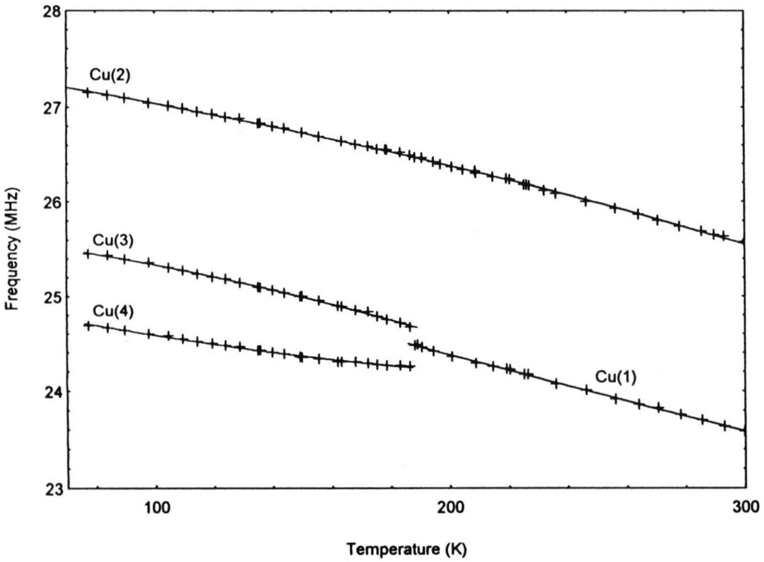


Fig. 3. Temperature dependence of the ^{63}Cu NQR frequencies of **1**.

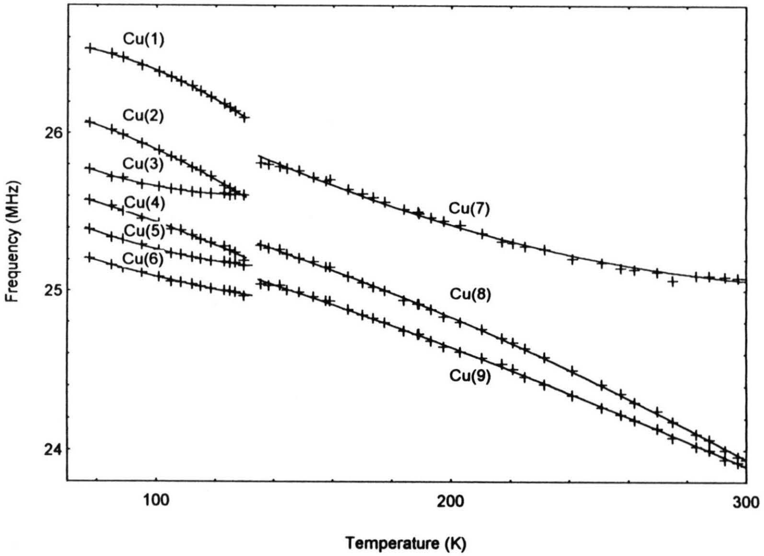


Fig. 4. Temperature dependence of the ^{63}Cu NQR frequencies of **2**.

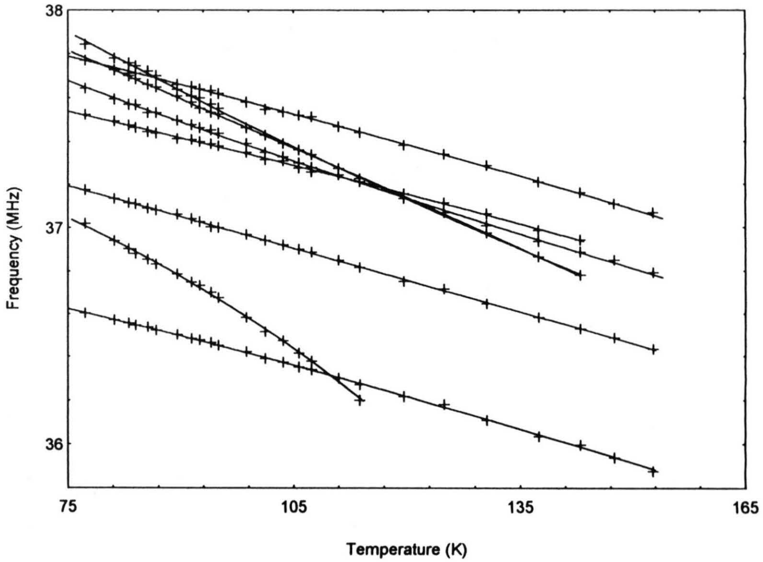


Fig. 5. Temperature dependence of the ^{35}Cl NQR frequencies of **1**.

Table 4. ^{63}Cu NQR frequencies and their temperature dependence. In all cases the corresponding ^{65}Cu NQR frequencies were observed at frequencies equal to 0.925 times that of the corresponding ^{63}Cu nucleus.

Complex	ν_{77} (MHz)	ν_0 (MHz)	A kHz K^{-1})	B (Hz K^{-2})	Range (K)
1					
Cu(1)		26.141	−9.402	2.945	188−300
Cu(2)	27.148	27.512	−3.809	−9.238	77−300
Cu(3)	25.456	25.756	−2.407	−17.738	77−187
Cu(4)	24.690	25.214	−7.574	13.006	77−187
2					
Cu(1)	26.529	26.386	7.765	−76.442	77−130
Cu(2)	26.066	26.305	0.438	−45.265	77−130
Cu(3)	25.770	25.567	−14.538	55.436	77−130
Cu(4)	25.574	25.829	−1.259	−26.649	77−130
Cu(5)	25.392	26.156	−13.208	43.078	77−130
Cu(6)	25.208	25.789	−9.353	24.072	77−130
Cu(7)		27.275	−13.082	18.984	135−302
Cu(8)		25.980	−3.633	−10.536	135−302
Cu(9)		25.815	−4.813	−5.259	135−302

Table 5. ^{35}Cl NQR frequencies and their temperature dependence of the chloroform solvent molecule in **1**. In all cases the corresponding ^{37}Cl NQR frequencies were observed at frequencies equal to 0.788 times that of the corresponding ^{35}Cl nucleus.

ν_{77} (MHz)	ν_0 (MHz)	A(kHz K^{-1})	B(Hz K^{-2})	Range(K)
37.842	39.422	−22.335	27.194	77−143
37.769	38.342	−6.366	−13.225	77−153
37.769	38.833	−12.682	−11.849	77−143
37.644	38.748	−15.578	17.959	77−153
37.526	38.075	−6.236	−11.843	77−143
37.526	38.297	−10.012	1.165	77−153
37.175	37.894	−9.083	−3.207	77−153
37.019	37.445	5.406	−142.87	77−114
36.602	37.161	−6.005	−15.504	77−153

of the resonance frequencies over the temperature ranges corresponding to the high- and low-temperature phases was fitted to a quadratic equation

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

The coefficients of these equations are shown in Table 4, together with the values of the resonance frequencies measured at 77 K.

For **1** it was also possible to observe nine distinct ^{35}Cl NQR frequencies of the solvent molecule from 77 K to just below the temperature of the transition to the high-temperature phase (Figure 5). Table 5 shows these frequencies at 77 K and the coefficients of their quadratic temperature dependence. It did not prove possible to observe the corresponding resonance frequencies for 1,2-dichloroethane in **2.**

Discussion

NQR

Both ^{63}Cu and ^{35}Cl have $I = 3/2$, so that each nucleus in a chemically-distinct environment gives rise to one resonance frequency that is related to the coupling constant, $e^2 Q q_{zz}$, and the asymmetry parameter, η, by the equation

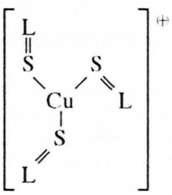
$$\nu = \frac{e^2 Q q_{zz}}{2} \sqrt{\left(1 + \frac{\eta^2}{3}\right)}, \tag{1}$$

where the asymmetry parameter lies in the range $0 \le \eta \le 1$ and is defined as

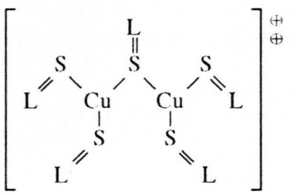
$$\eta = \frac{q_{xx} - q_{yy}}{q_{zz}} .$$

It is only possible to separate the two terms of (1) by studying the effect of a small magnetic field on the NQR spectrum of a large ($\gg 1$ g) single crystal of the sample. For asymmetry-parameters as large as 0.3 the coupling constant differs from twice the resonance frequency by only 1.5% but an asymmetry parameter of 1.0 increase the effect to 15%.

The ^{63}Cu resonance frequencies deserve comment inasmuch as they are the only examples that are known for three-coordinated Cu(I) complexes coordinated to two sulphur atoms and one nitrogen atom. The effect of a sulphur ligand on the ^{63}Cu resonance frequency of a three-coordinated Cu(I) complex may be seen from the results [14] for the complexes of the ligand methylimidazoline-2-(3H)-thione, (mimth).



A



B

The ^{63}Cu NQR frequency of A, Cu(mimth)$_3$NO$_3$, which has a mononuclear three-coordinated structure, [15], is 32.549 MHz while those B, Cu$_2$(mimth)$_5$SO$_4$ · 3 H$_2$O, where one of the five sulphur ligands bridges the two three coordinated copper atoms in the binuclear complex cation [16], are 27.926, and 27.285 MHz [14]. It may therefore be anticipated that a three-coordinated thione complex with two bridging ligands would have a resonance frequency as low as 22.5 MHz. The effect of changing the non-bridging ligand to an aromatic amine can be estimated as an increase of about 4.0 MHz from the fact that the frequencies of three-coordinated complex cations analogous to A, where the ligand is a substituted pyridine molecule such as 2,6-lutidine, are in the range 42–46 MHz [3]. The frequencies observed here are thus roughly those that would be expected.

The ^{35}Cl frequencies of the included chloroform molecules are similar to those of crystalline chloroform (38.308, 38.254 MHz at 77 K [17]) while their high temperature dependence is undoubtedly due to the considerable mobility that is often found for small molecules included in the lattice of a large host [18]. The nine distinct resonances of similar intensities probably arise from the existence of three different and asymmetric sites for the included solvent. The absence of resonances from the guest dichloroethane in **2** even in the low temperature phase is presumably due either to its excessively high mobility or to a static disorder. Some evidence of this may be seen in the results of the room-temperature structure of **2** as discussed above.

Both compounds exhibit a phase change between room-temperature and 77 K, at approximately 188 K for **1** and 133 K for **2** (Figures 3 and 4). In both cases this phase change may be associated with the loss of a symmetry-element in the room-temperature phase. In **1** at room temperature the hexanuclear complex has a center of symmetry and a plane of symmetry. This has the consequence that there are only two distinct copper sites, four copper atoms at one site and two at the other. In agreement with this, the room-temperature resonance at 23.6 MHz has twice the intensity of that at 25.8 MHz At 188 K the most intense resonance splits into two while the temperature-dependence of the high-frequency line shows no discernible discontinuity. Although it was not possible to observe the ^{35}Cl resonances of the chloroform molecule in the high-temperature phase, presumably because of rapid molecular reorientation, the crystallographic study shows that there are three sites for the chloroform molecule. One of the chlorine molecules lies on the mirror plane, and thus would yield only two distinct resonances of intensity-ratio 2:1, and two other sites, while not lying on the mirror plane, are related to each other by the corresponding symmetry-operation. This site thus corresponds to only one distinct chloroform molecule which would thus exhibit three chlorine resonances of equal intensity in the ratio 2:2:2. On the assumption that the mirror-plane is absent in the low-temperature phase, all three chlorine atoms in the three sites would reside in different crystallographic environments and would thus, in agreement with observation, yield nine distinct resonance frequencies. In agreement with the absence of ^{35}Cl resonances in the high-temperature phase, all nine resonances exhibit a large negative temperature coefficient and disappear before the phase-change (Fig. 5). In **2** the hexanuclear complex lies on a center of symmetry; there are therefore just three ^{63}Cu resonances. The appearance of six resonances at 133 K is thus consistent with the loss of the center of symmetry in the low-temperature phase.

Acknowledgements

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