Nuclear Quadrupole Resonance of Several Copper(I) Complexes with Heterocyclic Thioamido Ligands. Crystal structure of Chlorobis[tetrahydro-1*H*-pyrimidine-2-thione]copper(I) †

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The ^{63}Cu and ^{65}Cu n.q.r. spectra of the copper(I)–chloride and –bromide complexes of imidazolidine-2-thione (izt) and tetrahydro-1*H*-pyrimidine-2-thione (tpt), and the crystal structure of the complex [Cu(tpt)$_2$Cl] are reported. The n.q.r. data indicate that there is no phase change in the 77—300 K temperature interval. The compound [Cu(tpt)$_2$Cl] crystallizes in space group $P4_12_12$ with $a = b = 7.803(2)$, $c = 22.093(7)$ Å, and $Z = 4$. The structure has been solved by standard methods with a final R of 0.047. The complex is mononuclear and contains only one kind of Cu^I atom which is trigonally co-ordinated by two tpt molecules (Cu–S 2.206 Å) and one chlorine atom (Cu–Cl 2.317 Å). The conformation of the complex molecule is influenced by two intramolecular N–H · · · Cl hydrogen bonds.

Copper(I) complexes with soft donor ligands give rise to a wide range of stoicheiometries and configurations:[1] compounds may even present a different stereochemistry with the same stoicheiometry and, for instance,[2] they may exhibit two kinds of co-ordination for the central metallic atom in the same adduct. With this in mind, several spectroscopic studies have been carried out, the determination of the crystal structures by *X*-ray diffraction often bringing about the ultimate structural decision.[3,4] In this context, the potential of nuclear quadrupole resonance (n.q.r.) in providing important insights into the nature of the electronic distribution around quadrupolar nuclei (here namely ^{63}Cu and ^{65}Cu) has also been recognised for some copper complexes: thus a recent Zeeman effect study has been published for the trigonal site of several Cu^I phosphine complexes,[5] while other data for Cu^I co-ordination compounds with substituted thioureas,[6,7] phosphines,[8] and arsines[9] are available. However, application of this branch of spectroscopy to this class of compounds has been limited, in our opinion, by the lack of reference studies in conjunction with crystallographic determinations in order to mark out safely the boundary of the resonance area of the trigonal or tetragonal sites. For these reasons it was decided that a study of other Cu^I compounds by a joint n.q.r. and *X*-ray diffraction investigation would be of interest and derivatives of imidazolidine-2-thione (izt) and tetrahydro-1*H*-pyrimidine-2-thione (tpt) were chosen to be the subject of this investigation.

Experimental

Compounds.—All the complexes used in this study were prepared and purified according to published methods.[10,11] The products so obtained were identified on the basis of their elemental analysis and their i.r. and n.m.r. spectra as compared with the literature data.[11]

Table 1. ^{63}Cu and ^{65}Cu n.q.r. frequencies for some copper(I) complexes at various temperatures *

Compound	Temp. (K)	ν(^{63}Cu)	ν(^{65}Cu)
[{Cu(izt)$_2$Cl}$_2$]	77	28.73 {4}	26.59 {2}
	273	27.96 {6}	25.87 {3}
[{Cu(izt)$_2$Br}$_2$]	273	32.15 {3}	
[Cu(tpt)$_2$Cl]	77	31.06 {14}	28.75 {7}
	273	29.82 {30}	27.56 {13}
[Cu(tpt)$_2$Br]	77	28.21 {3}	26.10 {1.5}
	273	27.56 {5}	25.51 {2}

* Frequencies are given in MHz and are estimated to be within ±5 kHz. The ratios (^{63}Cu)/(^{65}Cu) are found to be in good agreement with the ratio of quadrupole moment $Q_{63}/Q_{65} = 1.0806$. Values in braces are peak-to-peak signal to peak-to-peak noise ratios obtained with 10 and 8 s recording time constants in series.

N.Q.R. Spectroscopy.—All n.q.r. spectra were recorded on a modified Decca spectrometer, details of which have been given elsewhere.[12] The ^{63}Cu and ^{65}Cu resonance frequencies were systematically measured at two fixed temperatures (77 and 273 K); the experimental values are reported in Table 1. In the case of [{Cu(izt)$_2$Cl}$_2$], [Cu(tpt)$_2$Cl], and [Cu(tpt)$_2$Br], a more complete temperature survey was carried out with the spectrometer probe fitted on a special ' L'Air Liquide-SMC ' cryostat.

X-Ray Structure Determination of [Cu(tpt)$_2$Cl].—A colourless single crystal was introduced, under a dry nitrogen atmosphere, into a Lindemann tube which was then flame sealed. The specimen was mounted on a Syntex P2$_1$ four-circle automatic diffractometer. Diffracted intensities were recorded at room temperature for $2\theta < 47°$. Of the total 651 independent reflections, 592 with $I > 2.5\sigma(I)$ were used in the final refinement. Lorentz and polarization corrections were applied.

Crystal data. $C_8H_{16}ClCuN_4S_2$, $M = 331.38$, Tetragonal, space group $P4_12_12$, $a = b = 7.803(2)$, $c = 22.093(7)$ Å, $U = 1\,345.2(6)$ Å^3, $D_m = 1.67$ (flotation), $Z = 4$, $D_c = 1.64$ g cm^{-3}, Mo-K_α radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 20 cm^{-1}.

Structure solution and refinement. The structure was solved in the tetragonal $P4_12_12$ space group. A three-dimensional Patterson function yielded the position of the copper atom; the positions of the other non-hydrogen atoms were found by the application of direct methods using the program DIRDIF.[13] Subsequent full-matrix anisotropic least-squares refinements

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† *Supplementary data available* (No. SUP 23454, 7 pp.): structure factors, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

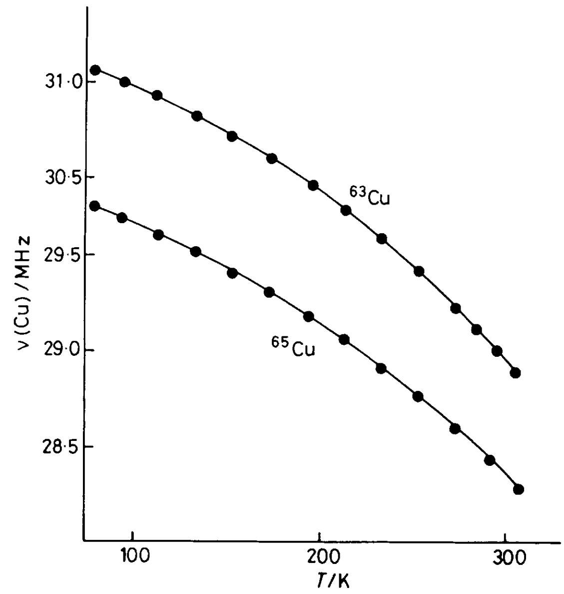

Figure 1. Temperature dependence plot of the ^{63}Cu and ^{65}Cu n.q.r. frequencies for [Cu(tpt)$_2$Cl]

were performed using the program SHELX 76.[14] Positions of the N(1) and N(3) hydrogen atoms were then determined from a difference map; the remaining hydrogens were included at positions calculated for rigid-group atoms. Full-matrix anisotropic least-squares refinement of non-H atoms yielded a final *R* of 0.047. Copper scattering factors were those of Cromer and Waber.[15]

Results and Discussion

Nuclear Quadrupole Resonance Spectroscopy.—For each of the four complexes [{Cu(izt)$_2$Cl}$_2$], [{Cu(izt)$_2$Br}$_2$], [Cu(tpt)$_2$Cl], and [Cu(tpt)$_2$Br] one single ^{63}Cu n.q.r. line has been detected at two fixed temperatures (77 and 273 K). Temperature variations of the ^{63}Cu frequencies were studied in each case from 77 up to 300 K. There is no evidence of any phase change in this temperature interval since the temperature dependence curves (Figure 1) do not show any discontinuities.

For the two izt complexes, the observation of copper quadrupole resonances has already been reported[6] without any temperature reference. However, these results are in good agreement with our own temperature determinations at 300 K.

Although only one ^{63}Cu signal has been detected, *X*-ray structural analysis of [{Cu(izt)$_2$Cl}$_2$] nevertheless shows[2] that this complex is binuclear and contains two types of copper(I) atoms: one tetrahedrally co-ordinated (three ligand molecules plus one chloride ion), and the other trigonally co-ordinated (two ligand molecules plus one chloride ion). A tentative explanation of the absence of an additional n.q.r. signal in the low-frequency area may lie in the fact that the quadrupole coupling constant of a perfect tetrahedral atom will be zero at a site of very high symmetry. However, according to the *X*-ray structure,[2] the tetragonally co-ordinated copper atom is far from occupying an ideal tetrahedral site; such examples have been already examined in the literature since, on the one hand, Negita *et al.*[5] have found ^{63}Cu n.q.r. lines at 13—16 MHz corresponding to pseudo-tetrahedral copper atoms in [Cu$_2$X$_2$(PPh$_3$)$_3$] (X = Cl, Br, or I) and, on the other hand, Valigura *et al.*[8] have also mentioned ^{63}Cu resonances for tetrameric [{CuX(PR$_3$)}$_4$] and [{CuX(AsR$_3$)}$_4$] (X = Cl, Br, or I; R = Et) complexes in the 9—13 MHz region. For these reasons, after several careful scans in the low-frequency area (down to 5 MHz) without any positive results, we decided that an *X*-ray diffraction study of the derivative [Cu(tpt)$_2$Cl] would be of interest.

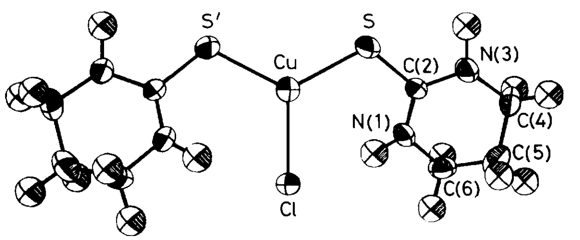

Figure 2. Molecular structure of [Cu(tpt)$_2$Cl] as drawn by the ORTEP program. Atoms are represented by their ellipsoids of thermal vibration drawn to enclose 50% of the electron density. The atom-labelling scheme is defined

Table 2. Fractional atomic co-ordinates (× 10^4) for [Cu(tpt)$_2$Cl] with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu	236(3)	236(3)	0
Cl	2 336(6)	2 336(6)	0
S(2)	1 022(7)	−2 444(6)	154(2)
N(1)	3 703(21)	−1 117(23)	742(7)
N(3)	3 659(20)	−4 038(20)	626(6)
C(2)	2 961(22)	−2 502(19)	530(6)
C(4)	5 323(27)	−4 252(27)	918(9)
C(5)	6 351(30)	−2 603(29)	886(9)
C(6)	5 292(26)	−1 147(25)	1 096(8)
H(1)	3 468(279)	−61(279)	588(85)
H(3)	2 655(298)	−5 039(282)	598(74)
H(41)	5 117(27)	−4 583(27)	1 387(9)
H(42)	6 027(27)	−5 267(27)	698(9)
H(51)	6 735(30)	−2 391(29)	422(9)
H(52)	7 477(30)	−2 700(29)	1 169(9)
H(61)	5 992(26)	32(25)	1 030(8)
H(62)	4 996(26)	−1 300(25)	1 571(8)

Description of the Structure of [Cu(tpt)$_2$Cl].—The structure of the tpt complex as drawn by the ORTEP program is presented in Figure 2, which also defines the atomic numbering scheme. The atomic co-ordinates are given in Table 2. A stereoscopic view of the contents of the unit cell is given in Figure 3.

The asymmetric unit of the structure comprises one half of the formula unit. The complex copper species lie with the copper–chlorine atoms situated on a crystallographic two-fold axis so that the two ligands are symmetrically related, consistent with the formulation of the complex as [Cu(tpt)$_2$Cl]. The structure then consists of discrete [Cu(tpt)$_2$Cl] molecules which are separated by ordinary van der Waals distances. The complex is mononuclear with only one independent copper atom exhibiting almost perfect trigonal planar co-ordination. Each copper atom is co-ordinated to two sulphur atoms of two different ligand molecules and one chlorine; the same co-ordination was previously observed by Devillanova and co-workers[4,16] in two *N*-substituted imidazolidine-2-thione copper(I) complexes.

These general *X*-ray data are perfectly consistent with the above n.q.r. analysis which assigned only one copper site to the asymmetric unit of the cell; besides, the joint *X*-ray and n.q.r. results obtained on the very same sample decisively assigned the high-frequency area (~30 MHz) to the quadrupole resonances of copper(I) nuclei occupying trigonal sites.

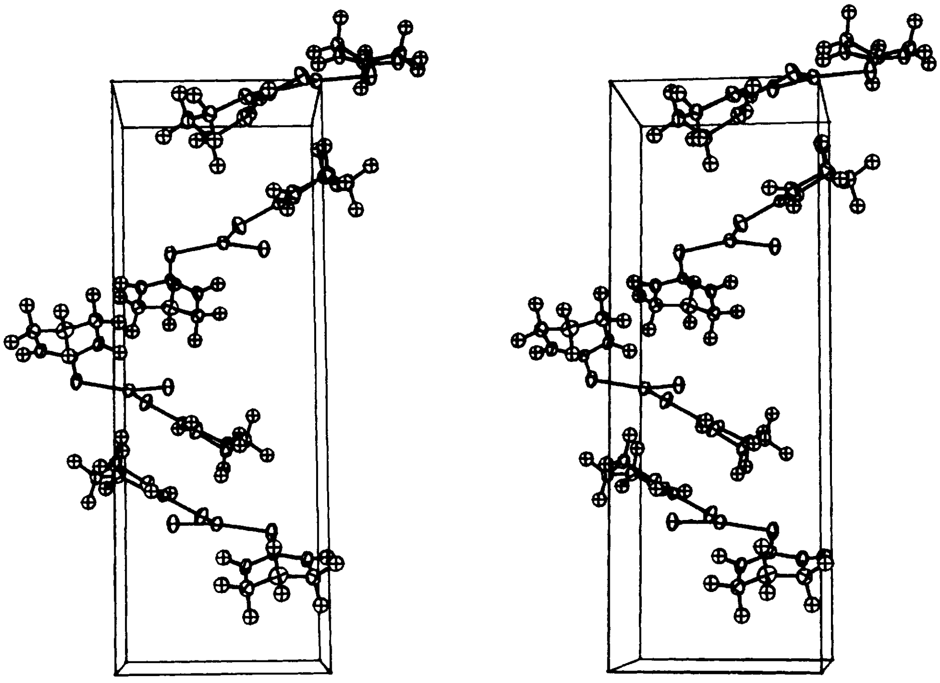

Figure 3. Stereoscopic view of the unit-cell packing for [Cu(tpt)$_2$Cl]

Table 3. Bond distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances			
Cu-Cl	2.317(3)	N(3)-C(4)	1.460(10)
Cu-S(2)	2.206(2)	N(3)-H(3)	1.108(90)
S(2)-C(2)	1.727(7)	N(1)-C(6)	1.467(10)
C(2)-N(3)	1.333(9)	N(1)-H(1)	0.910(84)
C(2)-N(1)	1.312(9)	C(4)-C(5)	1.518(12)
		C(5)-C(6)	1.480(12)
(*b*) Angles			
Cl-Cu-S(2)	118.3(1)	N(3)-C(2)-N(1)	120.2(6)
Cu-S(2)-C(2)	110.0(2)	C(2)-N(3)-C(4)	122.5(6)
S(2)-Cu-S(2')	123.4(1)	C(2)-N(1)-C(6)	123.4(6)
N(3)-C(2)-S(2)	117.2(5)	C(4)-C(5)-C(6)	109.9(7)
N(1)-C(2)-S(2)	122.5(5)	N(3)-C(4)-C(5)	110.6(6)
		N(1)-C(6)-C(5)	108.5(6)

Table 4. Selected planes in the form $Ax + By + Cz = D$ with deviations (Å) from the planes in square brackets

	A	*B*	*C*	*D*
Plane 1 (co-ordination plane)				
	−0.9659	0.9659	21.7518	0.0002
[Cu 0.000, Cl 0.000, S(2) 0.000, S(2') 0.000]				
Plane 2 (ligand plane)				
	3.8441	0.8851	−19.062	−0.1161
[S(2) −0.001, N(1) 0.026, N(3) −0.028, C(2) 0.022, C(4) 0.036, C(6) −0.040]				

Dihedral angle between planes 1–2 = 27.3°.

Several other features of the structural data are noteworthy. The bond distances between the central metal atom and the sulphur and chlorine ligands are in general agreement with those found previously in similar compounds; the Cu–S distance is relatively short (2.206 Å) (Table 3) and appears typical of trigonal three-co-ordinate planar Cu–S bonds;[2,5,16] on the other hand, the Cu–Cl distance (2.317 Å) is significantly longer than the corresponding distances in other substituted thiourea complexes mentioned above (2.25 [16] and 2.23 [5]).

Of general structural interest is the involvement of the N(1)–H of the two ligands in hydrogen bonding with the chlorine atom (N–H · · · Cl = 3.33 Å). In order to accommodate these two intramolecular bonds each ligand molecule is symmetrically twisted out of the 'co-ordination' plane determined by Cu, Cl, and the two S atoms. The dihedral angle between the tpt plane (determined by the sulphur and nitrogen atoms) and the co-ordination plane is close to 27° (see Table 4); the molecules adopt a 'propeller' shape configuration with the chlorine atom symmetrically interacting above and below the co-ordination plane with the two N(1)–H groups. In this context, the CuSC angle of 110° reflects the distortions induced by the hydrogen bonding.

Finally, a particularly interesting feature of this structure concerns the packing of molecules in the lattice (see Figure 3); the stereoscopic view of the unit cell reveals that the [Cu(tpt)$_2$-Cl] entities are roughly stacked in the shape of a helix along the *c* axis.

References

1 F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 4th edn., Wiley, New York, 1980, pp. 804—811.

2 L. P. Battaglia, A. Bonamarti Corradi, M. Nardelli, and M. E. Vidoni Tani, *J. Chem. Soc., Dalton Trans.*, 1976, 143.

3 See for example, I. F. Taylor, M. S. Weininger, and E. L. Amma, *Inorg. Chem.*, 1974, **13**, 2835 and refs. therein.

4 F. A. Devillanova, G. Verani, L. P. Battaglia, and A. Bonamarti Corradi, *Transition Met. Chem.*, 1980, **5**, 362.

5 H. Negita, M. Hiura, K. Yamada, and T. Okuda, *J. Mol. Struct.*, 1980, **58**, 205.

6 J. D. Graybeal and S. D. Ing, *Inorg. Chem.*, 1972, **11**, 3104.

7 Y. Himaya, N. Watanabe, and E. Niki, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2986.

8 D. Valigura, L. Verdonck, and G. P. van der Kelen, *Bull. Soc. Chim. Belg.*, 1980, **89**, 831.

9 G. Jugie, M. Durand, J. Ribas, and R. Mathieu, *J. Chem. Soc., Chem. Commun.*, 1981, 903.

10 G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1928, 143.

11 P. Castan, *Transition Met. Chem.*, 1981, **6**, 17.

12 J. C. Carter, G. Jugie, R. Enjalbert, and J. Galy, *Inorg. Chem.*, 1978, **17**, 1248.

13 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Th. E. M. van den Hark, and P. A. J. Prick, DIRDIF Technical Report 1980/1, Crystallography Laboratory, Toernooiveld, 6525 Ed. Nijmegen, Netherlands.

14 G. M. Sheldrick, SHELX program for crystal structure determination, Cambridge University, 1976.

15 D. T. Cromer and J. T. Waber, in ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974.

16 L. P. Battaglia, A. Bonamarti Corradi, F. A. Devillanova, and G. Verani, *Transition Met. Chem.*, 1979, **4**, 264.

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