Magnetism and Structure of Copper(II) Co-ordination Compounds. *X*-Ray Structure Determination of *trans*-Dichlorobis(*N*-methylimidazole)-copper(II)

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Two modifications of the title compound have been synthesized and the crystal and molecular structure of one has been determined by a single-crystal analysis using three-dimensional *X*-ray data. The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units in a unit cell of dimensions $a = 7.632(3)$, $b = 8.166(9)$, $c = 10.232(3)$ Å, $\alpha = 87.84(5)$, $\beta = 82.77(2)$, and $\gamma = 76.12(5)°$. The structure has been determined by direct methods and refined by least-squares techniques to $R = 0.041$ and $R' = 0.049$ for 2 307 reflections. It consists of discrete monomeric $CuCl_2(mim)_2$ units with tetrahedrally distorted *trans*-square-planar geometries around copper(II) The Cu–Cl distances [2.260(3) and 2.256(2) Å] are normal for terminal Cu–Cl bonds. The Cu–N distances [1.962(4) and 1.975(5) Å] are in the range expected for this type of compound. The two different crystal forms appear to have only slightly different spectroscopic and magnetic properties but totally different *X*-ray powder patterns.

SEVERAL compounds in the series CuX_2L_2 [L is a (substituted) pyridine or azole ligand and X = Cl or Br] have been investigated both structurally and magnetically in recent years.[1-7] All of the structurally established compounds containing pyridine ligands show rather strong magnetic superexchange interactions which result in the observation of broad maxima in the susceptibility–temperature curves, at low temperatures. Much effort has been undertaken to predict the structure from magnetic and spectroscopic data, however, until now, it has not been possible to predict structural data in a quantitative way. One of the reasons for this failure is that it was not clear which factors govern the kind and magnitude of the magnetic superexchange interactions in this class of one-dimensional transition-metal co-ordination compound.

Recently we reported on some compounds in which only very weak superexchange interactions exist.[7] One of these, dichlorobis(*N*-methylimidazole)copper(II), abbreviated as $[CuCl_2(mim)_2]$, showed a very small interaction between the copper(II) ions, and since the geometry of a chain exhibiting an exchange value near zero is highly interesting an *X*-ray investigation has now been undertaken. In addition, some other compounds, which could not be prepared as single crystals suitable for a complete structure determination, have been investigated by powder-diffraction techniques and/or Weissenberg photographs, in order to obtain information about the shortest crystal axis. For the chain compounds that have been investigated structurally, one short crystal axis in the vicinity of 4.0 Å (equal to the M–M distance) was always found.[1-4,8-11]. The present compound, unfortunately, has no Cu–Cl–Cu bridges, explaining the observed absence of, or at best very weak, magnetic interactions.[7]

EXPERIMENTAL

Synthesis.—The compound $[CuCl_2(mim)_2]$ was prepared by mixing alcoholic solutions of $CuCl_2 \cdot 6H_2O$ and *N*-methylimidazole (mim) as previously described.[7] Repeated synthesis resulted in two different species with chemical formula $CuCl_2(mim)_2$ (see below).

Crystal Structure and Molecular Geometry.—*Crystal data.* $C_8H_{12}Cl_2CuN_4$, $M = 298.67$, Triclinic, $a = 7.632(3)$, $b = 8.166(9)$, $c = 10.232(3)$ Å, $\alpha = 87.84(5)$, $\beta = 82.77(2)$, $\gamma = 76.12(5)°$, $U = 614.1$ Å^3, $D_m = 1.62$ g cm^{-3}, $Z = 2$, $D_c = 1.615$ g cm^{-3}, $F(000) = 302$, $\lambda(\text{Mo-}K_\alpha) = 0.710\ 69$ Å, $\mu(\text{Mo-}K_\alpha) = 22.5$ cm^{-1}, space group $P1$ or $P\bar{1}$, shown to be $P\bar{1}$ from the structure determination.

Intensity Data Collection.—A suitable specimen, a rectangular parallelepiped measuring 0.11 × 0.21 × 0.29 mm, was mounted on an Enraf–Nonius CAD 4 diffractometer and *X*-ray intensity data were measured in the ω—2θ scan mode, by use of monochromated Mo-K_α radiation ($2\theta_{mon.}$ 12.8°). Accurate unit-cell parameters and the orientation matrix were determined from a least-squares treatment of the angular settings of eight reflections. The standard deviations of the lattice parameters were obtained from a comparison of the deviations from integer values of the indices, calculated with the orientation reflections as described by Duisenberg.[12] Intensity data were collected for a redundant set of 2 993 reflections to $\theta_{max.}$ 27.5°. A standard reflection was measured every 30 min of *X*-ray exposure time, and a smooth function through these values was used to correct for fluctuations in the intensity data (3%). Averaging of equivalent data resulted in a set of 2 810 unique reflections of which 2 307 had intensities above background [$I > 2.5\sigma(I)$]. Intensities were corrected for Lorentz and polarization effects.

Structure Determination and Refinement.—The data were converted into normalized structure magnitudes and the structure solved by direct methods for the heavy atoms. The positions of the other atoms were found by application of standard Fourier techniques. These positions and anisotropic factors were refined by block-diagonal least-squares techniques to a final $R = 0.041$, $R' = 0.049$.† Unit weights were used throughout the refinement. A final difference-Fourier map only showed possible hydrogen

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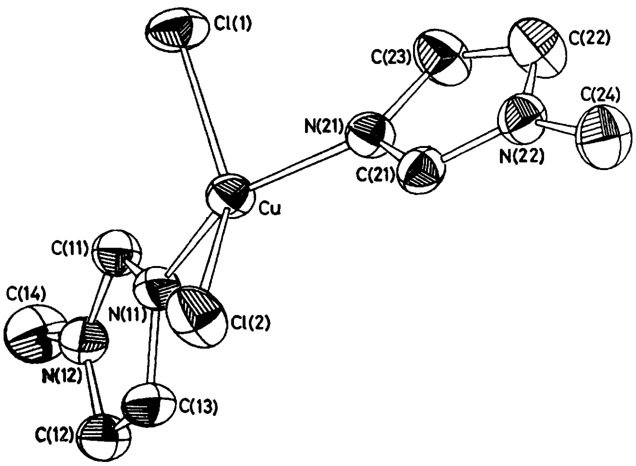
† The function minimized was $\Sigma[w(|F_o| - |F_c|)]^2$. The refinement was on F. The weighted and unweighted residuals are defined as $R = (\Sigma|F_o| - |F_c|)/(\Sigma|F_o|)$ and $R' = [\Sigma w(|F_o| - |F_c|)^2]/(\Sigma w|F_o|^2)^{\frac{1}{2}}$.

positions, however no attempts were made to include these in the calculations. At the end of refinement all parameter shifts were $<0.6\sigma$. Programs used in this structure determination include MULTAN 77,[13] '*X*-RAY '76',[14] and ORTEP.[15] Final positional parameters are listed in Table 1. Atomic scattering factors for Cu, Cl, N, and C were taken from ref. 16. Observed and calculated structure factors as well as final anisotropic thermal parameters are listed in Supplementary Publication No. SUP 22505 (23 pp.).†



ORTEP drawing scaled to include 40% probability and showing the labelling scheme for $[CuCl_2(mim)_2]$

TABLE 1

Final refined co-ordinates for the non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Cu	0.321 2(1)	0.264 5(1)	0.218 4(1)
Cl(1)	0.197 2(2)	0.517 9(2)	0.131 2(1)
Cl(2)	0.280 8(2)	0.082 4(2)	0.384 3(1)
N(11)	0.259 9(5)	0.130 8(5)	0.083 0(4)
N(12)	0.193 9(5)	0.057 6(5)	−0.106 3(4)
C(11)	0.203 8(7)	0.187 1(6)	−0.031 4(5)
C(12)	0.245 2(7)	−0.089 6(6)	−0.034 9(5)
C(13)	0.285 9(7)	−0.044 2(6)	0.081 6(5)
C(14)	0.141 1(9)	0.071 6(8)	−0.240 3(6)
N(21)	0.504 9(5)	0.348 4(5)	0.298 4(4)
N(22)	0.716 4(5)	0.363 4(5)	0.420 5(4)
C(21)	0.577 9(6)	0.292 0(6)	0.408 1(5)
C(22)	0.732 7(9)	0.470 2(8)	0.315 5(6)
C(23)	0.601 3(8)	0.461 8(7)	0.239 1(6)
C(24)	0.830 2(8)	0.330 9(8)	0.530 2(6)

RESULTS AND DISCUSSION

Description and Discussion of the Structure.—The unit cell of *trans*-dichlorobis(*N*-methylimidazole)copper(II) consists of two discrete monomeric $CuCl_2(mim)_2$ units. The Figure shows one such molecular unit. The geometry about each copper ion is best described as tetrahedrally distorted square planar. Interatomic distances, angles, and planes of interest are given in Tables 2 and 3.

TABLE 2

Bond distances (Å) and angles (°)

Cu–Cl(1)	2.260(3)	Cl(1)–Cu–Cl(2)	143.57(6)
Cu–Cl(2)	2.256(2)	Cl(1)–Cu–N(11)	95.4(1)
Cu–N(11)	1.962(4)	Cl(1)–Cu–N(21)	94.0(1)
Cu–N(21)	1.975(5)	Cl(2)–Cu–N(11)	94.9(1)
		Cl(2)–Cu–N(21)	94.4(1)
		N(11)–Cu–N(21)	149.7(1)
N(11)–C(11)	1.325(6)	Cu–N(11)–C(11)	126.5(3)
C(11)–N(12)	1.351(7)	Cu–N(11)–C(13)	126.7(3)
N(12)–C(12)	1.382(6)	Cu–N(21)–C(21)	127.2(4)
N(12)–C(14)	1.470(7)	Cu–N(21)–C(23)	125.1(3)
C(12)–C(13)	1.356(8)		
C(13)–N(11)	1.395(6)	C(11)–N(11)–C(13)	106.4(4)
		N(11)–C(11)–N(12)	110.6(4)
N(21)–C(21)	1.333(6)	C(12)–N(12)–C(12)	107.6(4)
C(21)–N(22)	1.345(7)	C(11)–N(12)–C(14)	125.9(4)
N(22)–C(22)	1.371(7)	C(12)–N(12)–C(14)	126.5(5)
N(22)–C(24)	1.482(8)	N(12)–C(12)–C(13)	106.6(4)
C(22)–C(23)	1.363(9)	N(11)–C(13)–C(12)	108.8(4)
C(23)–N(21)	1.392(8)		
		C(21)–N(21)–C(23)	107.1(5)
		N(21)–C(21)–N(22)	109.7(4)
		C(21)–N(22)–C(22)	108.4(5)
		C(21)–N(22)–C(24)	125.1(4)
		C(22)–N(22)–C(24)	126.5(5)
		N(22)–C(22)–C(23)	107.0(6)
		N(21)–C(23)–C(22)	107.9(5)

TABLE 3

Least-squares planes through the mim ring atoms

Plane	Atoms in plane	Other atoms	Distance [a]/ Å
I	N(11)	Cu	0.19
(0.003) [b]	N(12)	Cl(1)	−0.16
	C(11)	Cl(2)	−0.76
	C(12)	N(21)	1.33
	C(13)	C(14)	0.03
II	N(21)	Cu	−0.25
(0.002) [b]	N(22)	Cl(1)	1.04
	C(21)	Cl(2)	−0.27
	C(22)	N(11)	−1.39
	C(23)	C(24)	0.001

[a] From the calculated plane. [b] Standard deviation in Å.

The two Cu–Cl distances [2.260(3) and 2.256(2) Å] are typical for terminal Cu–Cl bonds. The shortest intermolecular separations are much greater than the sum of the van der Waals radii of the two atoms involved. From this fact it is evident that $[CuCl_2(mim)_2]$ does not belong to the $[CuCl_2(py)_2]$-type compounds (py = pyridine). The Cu–N distances [1.962(4) and 1.975(5) Å] are very close to the Cu–N bond length of 1.953(5) Å in $[CuBr_2(mim)_2]$.[4] The *cis* [94.0(1)—95.4(1)°] and *trans* angles [143.57(6) and 149.7(1)°] of all ligands around the copper ion are intermediate between the expected values for tetrahedral (109.47°) and square-planar geometries (90 or 180°) respectively. Comparable angles, deviating slightly more from the angles expected for tetrahedral geometries, occur in $[Cu(dmaep)Cl_2]$ [dmaep = 2-(2-dimethylaminoethyl)pyridine].[17] The geometry of the latter compound is described as pseudo-tetrahedral, as concluded from the electronic spectra; however, in the present case this conclusion could not be drawn (see above).

The carbon–carbon distances and angles within the two different mim ligands are similar, and very close to those reported for $[CuBr_2(mim)_2]$, *cis*-$[PtCl_2(mim)_2]$, and other metal compounds containing *N*-methylimidazole.[4,18] Least-squares planes through the ring atoms of mim are shown in Table 3. The methyl groups are almost within the plane, but the copper atom is displaced by 0.19 and 0.25 Å out of the least-squares planes, defined by respectively mim(1) and mim(2). Another

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

typical feature of the structure is that the chlorine atoms lie very close to the planes through the mim rings; Cl(1) has a distance to plane I of 0.16 Å and Cl(2) has a distance to plane II of 0.27 Å. The origin for this is not clear.

Spectroscopy.—Two modifications of [CuCl$_2$(mim)$_2$] were found (α,β), which have only slightly different i.r. spectra (see below) and magnetic susceptibilities. The α form, of which the *X*-ray determination is presented, could be isolated in a pure form, but the β form could not be prepared pure since its crystals were contaminated to some extent by the α form. On recrystallization of both forms from alcohol, the compound [CuCl$_2$(mim)$_2$] decomposed into a brown product of composition CuCl$_2$(mim). Despite careful investigations, no conditions could be found for the preparation of any of the modifications in a predictably pure form. The mim ligand has been shown to yield four different crystal modifications of the compound [PtCl$_2$(mim)$_2$].[18] This could be concluded from the totally different *X*-ray powder patterns and i.r. spectra.

The i.r. spectra of the present [CuCl$_2$(mim)$_2$] compounds show small differences, occurring at *ca.* 875 and 3 150 cm^{-1}. For the α modification the band at 3 150 cm^{-1} (C–H stretching vibration [18]) is split, whereas with the β modification this band does not split. In the spectrum of the β modification the band at 875 cm^{-1} (a C–H out-of-plane bending [18]) is very weak, whereas for the α modification this band is very strong. From these data it can be concluded that the mim ligands may have different orientations in the crystal structures. The *X*-ray powder-diffraction patterns of the two modifications are very different (Table 4). A possible reason for the occurrence of the different modifications could be the absence of hydrogen bonding, which results in only very weak (only van der Waals interactions) intermolecular forces and therefore small differences in packing energy between different ligand orientations. However, the ligand-field and e.s.r. spectra of both forms are very similar and have been described previously.[7] The magnetic-susceptibility measurements of the β modification showed very weak magnetic superexchange between adjacent copper(II) ions.[7] Measurements carried out on the α modification in the 4.2—100 K region did not show any magnetic interaction down to 4.2 K, *i.e.* the effective magnetic moment per copper(II) ion was temperature independent even at the lowest temperatures.

TABLE 4

d Values (Å) derived from the *X*-ray powder-diffraction patterns of the two crystal forms (only values higher than 2.5 Å have been tabulated)

α: 10.10w, 7.37w, 6.21vs, 5.68s, 5.06s, 4.82m, 4.28s, 4.15s, 3.95w, 3.70s, 3.39m, 3.18w, 2.98w, 2.77m, 2.63s

β: 8.62w, 7.37vs, 4.61vs, 4.41vs, 4.28s, 4.17s, 4.02w, 3.86m, 3.68vs, 3.63w, 3.56vs, 3.39s, 3.32m, 3.20s, 2.93m, 2.79m, 2.74s, 2.71s, 2.56m

As shown, the structurally investigated compound [CuCl$_2$(mim)$_2$] unfortunately consists of monomeric molecules and therefore is not interesting from a magnetic point of view. It is noted that, from this structure determination and the fact that the e.s.r. *g* values are very close to those observed for other geometries around Cu^{II}, it is evident that e.s.r. measurements on copper(II) compounds must be handled with great care when attempting to correlate them with structural details. For example, three structurally investigated copper(II) compounds having almost identical powder *g* values are known, *i.e.* [CuCl$_2$L$_2$] where L = 4-vinylpyridine [3] (*g* 2.26, 2.08, and 2.04 [6]), imidazole [19] (*g* 2.24, 2.09, and 2.03 [7]), and mim (*g* 2.27, 2.09, and 2.04 [7]). The geometries around Cu^{II} are best described as pseudo-elongated octahedral with two chloride bridges, distorted square pyramidal with one chloride bridge, and tetrahedrally distorted square planar respectively. Thus from e.s.r. powder data only it is not possible to predict the geometry around the copper(II) centre. Very recently, Hatfield and co-workers [11] published a 'reversed' e.s.r. spectrum (*i.e.* $g_{\parallel} < g_{\perp}$) for the compound [CuCl$_2$(thiazole)$_2$], although its structure is very similar to that of [CuCl$_2$(py)$_2$]. This unexpected e.s.r. spectrum can be explained by assuming strong exchange narrowing between different copper(II) sites, which could be confirmed only by the crystal-structure determination.[11]

Finally, we wish to report some results obtained from Weissenberg photographs of very thin needle-like single crystals and powder-diffraction data for the compounds [CuCl$_2$(Hpz)$_2$], [CuCl$_2$(4Me-py)$_2$], and [CuBr$_2$(3,5Me$_2$-py)$_2$].* All these compounds were shown to have a short crystal axis in the vicinity of 4.0 Å, which is indicative of the presence of [CuCl$_2$(py)$_2$]-like chain structures (see below). The existence of this short crystal axis in the pyrazole compound [3.76(5) Å] is very promising, because the exchange interaction in this compound is very small.[7] The structural data should yield the bridge geometry responsible for the superexchange interaction of about zero. These data will give further insights into the problem of understanding structure–superexchange relations in one-dimensional copper(II) chain compounds. However, the single crystals of [CuCl$_2$(Hpz)$_2$] needed for a complete structure analysis have not yet been prepared.

The curve of magnetic susceptibility against temperature for [CuCl$_2$(4Me-py)$_2$] deviated strongly from the other compounds within the [CuCl$_2$L$_2$] (L = substituted pyridine) series.[5,6] Crawford and Hatfield [5] suggested that the structure of this compound consists of linear chains with alternating long and short Cu–Cu distances. However, from the 4.0(1) Å crystal axis presently observed it is evident that in this compound no alternating long and short Cu–Cu distances occur at room temperature, since this short crystal axis is equal to the Cu–Cu distance within the chain.[1-4,11] Since the preliminary results indicate that the susceptibility data for [CuCl$_2$(4Me-py)$_2$] over the temperature range 4.2—50.0 K can be fitted using an alternating-chain model, it may be

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* Hpz = Pyrazole, 4Me-py = 4-methylpyridine, and 3,5Me$_2$-py = 3,5-dimethylpyridine.

that the compound undergoes phase transition at some point.

The structure determination of [$CuBr_2(3,5Me_2\text{-}py)_2$] from *X*-ray powder data is in progress and preliminary results again show the existence of a short crystal axis [4.10(1) Å], which means that this compound also belongs to the [$CuBr_2(py)_2$] type, in agreement with the strong superexchange interactions observed.[6]

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