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Neutron Diffraction Structure Determination of Dichlorotetrapyrazolecopper(II), $Cu(C_3H_4N_2)_4Cl_2$

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The crystal and molecular structure of dichlorotetrapyrazolecopper(II), Cu(NHN:CHCH:CH)$_4$Cl$_2$, was determined by single-crystal neutron diffraction techniques. This compound crystallizes in the monoclinic system with a = 13·657 (5), b = 9·200 (5), c = 14·900 (5) Å, β = 118·04 (1)°, space group $C2/c$, ϱ_0 = 1·63 g cm^{-3} and Z = 4. The structure was refined by least-squares calculations to a conventional R value of 3% for 1143 reflections. The $Cu(C_3H_4N_2)_4Cl_2$ molecule is centrosymmetric with the Cu atom at the center of a distorted octahedron formed by two chlorine atoms and a nitrogen atom from each of four pyrazole rings. The accurate location of the hydrogen atoms shows that the conformation of the complex is due to intramolecular hydrogen bonding. The coordination distances Cu–Cl and Cu–N (2·84 and 2·02, 2·01 Å, respectively) are significantly different from those of the corresponding nickel analog (Ni–Cl and Ni–N 2·51; and 2·10, 2·09 Å, respectively).

Introduction

As part of a study of compounds with complex cations, the structure of dichlorotetrapyrazolecopper(II), Cu(Pz)$_4$Cl$_2$, (Pz = pyrazole, NHN:CHCH:CH) has been determined by single-crystal neutron diffraction methods.

The purpose of this investigation is to compare the structural features of Cu(Pz)$_4$Cl$_2$ with those of the related nickel complexes, Ni(Pz)$_4$Cl$_2$ and Ni(Pz)$_4$Br$_2$, whose structures have been determined by X-ray diffraction methods (Reimann, Mighell & Mauer, 1967; Mighell, Reimann & Santoro, 1969).

Neutron diffraction was used to assign unambiguously the carbon and nitrogen atoms of the pyrazole rings and to obtain accurate hydrogen atom parameters for detecting possible hydrogen bonding in the structure as postulated in the nickel analogs.

Experimental

Crystals of Cu(Pz)$_4$Cl$_2$ were grown by slow evaporation of an aqueous solution of CuCl$_2$ and pyrazole. The crystal data for this complex are reported in Table 1. The chemical analysis for copper, chlorine, carbon and nitrogen gave: Cl, 17·35%; Cu, 15·81%; C, 35·22%; N, 27·52%, in close agreement with the formula assigned from the complete structure determination. A piezoelectric test was negative.

Table 1. *Crystal data for dichlorotetrapyrazolecopper*(II), Cu(Pz)$_4$Cl$_2$

a = 13·657 (5) Å*	Space group $C2/c$†
b = 9·200 (5)	Z = 4
c = 14·900 (5)	ϱ_o = 1·63 g cm^{-3}‡
β = 118·04 (1)°	ϱ_c = 1·635 g cm^{-3}

Systematic extinctions

hkl,	$h+k=2n+1$
$h0l$,	$l=2n+1$

* The unit-cell dimensions were refined by least squares using X-ray powder data (Mo $K\alpha$ = 0·71069 Å).

† Assigned on the basis of the complete structure determination.

‡ Determined by the flotation method.

The crystal chosen for the neutron diffraction measurements was a prismatic needle approximately 5 mm long and between 1·5 and 2·0 mm in diameter. The needle axis was [001] and the prism was bounded by prominent, well formed {010} and {110} faces. It was mounted on a computer-controlled four-circle diffractometer at the National Bureau of Standards' research reactor (Alperin & Prince, 1970) with the needle axis approximately parallel to the φ axis of the diffractometer. Integrated intensities were measured by a procedure described previously (Prince, 1972) only if the intensity at the peak position exceeded that at background positions on either side by more than 2σ, where $\sigma=(I_p+I_b)^{1/2}$ and I_p and I_b are peak and background intensities, respectively. All reflections in the range $-5° \le \chi \le 90°$ and $2\theta \le 100°$ with a neutron wavelength of 1·232 Å were measured. All reflections except those of the type $h0l$ which had χ values greater than 5° were measured in at least two symmetry-related positions. The integrated intensities were converted to F values and merged to form a unique set. Of 1666 unique reflections within the limiting sphere, 1143 had observable intensities. The R index for equivalent reflections, defined by $R=\sum|F_{hkl}-F_{h\bar{k}l}|/\sum_{hkl}$, was 0·018.

Refinement

Space group and lattice parameters suggest that Cu(Pz)$_4$Cl$_2$ is isostructural with the nickel analog Ni(Pz)$_4$Cl$_2$. The initial refinement was therefore carried out by using the atomic parameters of the nickel complex. With this assumption, however, the structure did not refine to a satisfactory R value and some of the parameters for one of the pyrazole rings were very different from the expected values. At this stage, the atoms C(3) and N(2) in ring 1 were interchanged. With this assignment the refinement rapidly converged to a conventional R value of 4%. Neutron scattering amplitudes used were: Cu, 0·76; Cl, 0·96; N, 0·94; C, 0·665; H, −0·374 (Bacon, 1972).

The final stage of refinement was performed using the program *RFINE* (Finger, 1972), and included a secondary extinction parameter S of the form $F'_{\rm calc} = F_{\rm calc}(1+S\beta F^2_{\rm calc})^{-1/4}$, where $\beta=[2\lambda^2/(V^2 \sin 2\theta)]$ and V is the volume of the unit cell. S represents the product $\bar{T}r^*$, where $\bar{T}$ is an absorption averaged path length through the crystal, and is treated here as a constant, and r^* is a parameter with units of length. Weights for this stage of refinement were assigned by $w=1/\sigma^2$, and $\sigma=[\sigma^2_{\rm stat}+(0{\cdot}015F_{\rm obs})^2]^{1/2}$ where $\sigma_{\rm stat}$ is computed from counting statistics. Five cycles of refinement gave a weighted R index of 0·039 and an unweighted R of 0·030. There was no systematic variation of the goodness of fit as a function of $F^2_{\rm obs}$ or of $\sin \theta/\lambda$, and a difference Fourier map contained no features with amplitudes greater than 5% of the smallest atomic peaks in an $F_{\rm obs}$ synthesis. Observed and calculated structure factors, atomic parameters and thermal parameters are reported in Tables 2,† 3 and 4.

Table 3. *Atomic coordinates*

The numbers in parentheses are standard deviations in the last significant figures.

	X/a	Y/b	Z/c
Cu	0	0	0
Cl	0·0961 (1)	−0·1857 (1)	−0·0895 (1)
N(1)	0·1427 (1)	−0·0185 (1)	0·1322 (1)
N(2)	0·2318 (1)	−0·0960 (1)	0·1445 (1)
N(3)	0·0601 (1)	0·1705 (1)	−0·0428 (1)
N(4)	0·1107 (1)	0·1544 (2)	−0·1001 (1)
C(1)	0·3140 (2)	−0·0862 (2)	0·2412 (2)
C(2)	0·2754 (2)	0·0015 (2)	0·2935 (1)
C(3)	0·1673 (1)	0·0412 (2)	0·2216 (1)
C(4)	0·1345 (2)	0·2837 (2)	−0·1270 (2)
C(5)	0·0963 (2)	0·3891 (2)	−0·0859 (2)
C(6)	0·0506 (2)	0·3123 (2)	−0·0338 (1)
H(1)	0·3919 (4)	−0·1395 (6)	0·2649 (5)
H(2)	0·3202 (5)	0·0331 (8)	0·3714 (4)
H(3)	0·1072 (4)	0·1073 (5)	0·2297 (4)
H(4)	0·1752 (6)	0·2912 (6)	−0·1740 (6)
H(5)	0·1008 (5)	0·5061 (5)	−0·0920 (5)
H(6)	0·0110 (5)	0·3516 (5)	0·0096 (4)
H(7)	0·2300 (3)	−0·1502 (5)	0·0862 (4)
H(8)	0·1252 (4)	0·0509 (5)	−0·1151 (4)

Discussion

$Cu(Pz)_4Cl_2$ is centrosymmetric with the copper atom located at the center of symmetry and all other atoms in general positions. The asymmetric unit therefore contains one half of a copper atom, one chlorine atom and two pyrazole ligands. Fig. 1 shows a stereographic view of the molecule of $Cu(Pz)_4Cl_2$.

A comparison of the bond distances and angles of this structure with those of the related $Ni(Pz)_4Cl_2$ and $Ni(Pz)_4Br_2$ complexes is given in Tables 5 and 6. The bond distances of the pyrazole rings are similar in the three complexes but the coordination distances differ

Table 4. *Anisotropic thermal parameters*

The general anisotropic temperature factor has the form $\exp[-\frac{1}{4}(h^2a^{*2}B_{11}+k^2b^{*2}B_{22}+l^2c^{*2}B_{33}+2hka^*b^*B_{12}+2hla^*c^*B_{13}+2klb^*c^*B_{23})]$. The numbers in parentheses are standard deviations in the last significant figures.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	2·74 (8)	2·75 (8)	2·23 (7)	−0·78 (6)	0·78 (6)	0·60 (6)
Cl	3·58 (5)	2·94 (5)	3·25 (5)	0·41 (4)	1·92 (5)	−0·07 (4)
N(1)	2·54 (5)	2·67 (5)	2·29 (4)	−0·13 (3)	0·99 (4)	0·06 (3)
N(2)	3·17 (6)	3·04 (5)	3·54 (6)	−0·02 (4)	1·73 (5)	0·07 (5)
N(3)	2·98 (5)	2·48 (5)	2·85 (5)	−0·42 (4)	1·46 (4)	0·26 (4)
N(4)	4·29 (6)	2·97 (6)	4·07 (6)	−0·05 (4)	2·73 (5)	0·37 (4)
C(1)	2·74 (8)	3·75 (8)	3·90 (9)	0·42 (7)	1·02 (7)	0·89 (7)
C(2)	3·58 (9)	4·53 (9)	2·32 (8)	−0·15 (7)	0·61 (7)	0·32 (6)
C(3)	3·12 (7)	3·08 (7)	2·22 (7)	0·09 (6)	1·17 (6)	−0·18 (5)
C(4)	5·24 (10)	3·14 (8)	5·32 (11)	0·07 (7)	3·84 (9)	0·86 (7)
C(5)	4·65 (10)	2·62 (8)	5·16 (10)	−0·31 (6)	3·04 (9)	0·59 (7)
C(6)	3·60 (7)	2·67 (7)	3·82 (8)	−0·30 (6)	2·20 (7)	0·01 (6)
H(1)	3·7 (2)	7·0 (3)	8·3 (3)	1·8 (2)	1·8 (2)	1·3 (2)
H(2)	7·7 (3)	9·7 (4)	3·1 (2)	−0·3 (3)	0·6 (2)	−0·8 (2)
H(3)	5·5 (2)	5·7 (2)	5·4 (2)	1·2 (2)	2·9 (2)	−0·7 (2)
H(4)	11·9 (4)	6·4 (3)	11·0 (4)	−0·3 (3)	9·9 (4)	1·2 (3)
H(5)	9·4 (4)	3·1 (2)	10·2 (4)	−0·2 (2)	6·7 (3)	1·2 (2)
H(6)	9·0 (3)	4·4 (2)	8·3 (3)	−0·6 (2)	6·7 (3)	−0·9 (2)
H(7)	5·6 (2)	4·5 (2)	5·5 (2)	−0·3 (2)	3·5 (2)	−0·6 (2)
H(8)	7·6 (3)	3·9 (2)	7·2 (3)	0·1 (2)	5·2 (2)	0·0 (2)

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† Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31064 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

significantly. Specifically, for the chloride complexes, $Cu(Pz)_4Cl_2$ and $Ni(Pz)_4Cl_2$, the Cu–Cl distance is 2·84 Å compared to the Ni–Cl distance of 2·51 Å and the average Cu–N coordination distance is 2·02 Å compared to the average Ni–N distance of 2·09 Å (Jahn–Teller effect). Thus, in the coordination octahedron of the copper complex the metal–chlorine distances are longer and the metal nitrogen–distances are shorter than the corresponding distances in the related nickel complex. A similar comparison may be made between $Cu(Pz)_4Cl_2$ and $Ni(Pz)_4Br_2$.

Table 5. *Comparison of bond distances in* $Cu(Pz)_4Cl_2$, $Ni(Pz)_4Cl_2$ *and* $Ni(Pz)_4Br_2$

The numbers in parentheses are the standard deviations.

	$Cu(Pz)_4Cl_2$*	$Ni(Pz)_4Cl_2$†	$Ni(Pz)_4Br_2$†
Me–Cl(Br)	2·840 (1) Å	2·507 (1) Å	2·682 (1) Å
Me–N(1)	2·024 (1)	2·097 (2)	2·101 (4)
Me–N(3)	2·009 (1)	2·087 (2)	2·080 (5)
Ring 1			
N(1)–N(2)	1·347 (2)	1·345 (4)	1·338 (9)
N(2)–C(1)	1·351 (2)	1·357 (4)	1·362 (9)
C(1)–C(2)	1·385 (3)	1·371 (7)	1·356 (15)
C(2)–C(3)	1·405 (3)	1·393 (5)	1·383 (10)
C(3)–N(1)	1·330 (2)	1·329 (4)	1·326 (9)
C(1)–H(1)	1·070 (5)	–	
C(2)–H(2)	1·068 (5)	–	
C(3)–H(3)	1·072 (5)	–	
N(2)–H(7)	0·992 (5)	–	
Ring 2			
N(3)–N(4)	1·336 (2)	1·342 (6)	1·349 (14)
N(4)–C(4)	1·342 (2)	1·333 (6)	1·342 (13)
C(4)–C(5)	1·374 (3)	1·356 (6)	1·346 (16)
C(5)–C(6)	1·396 (3)	1·389 (6)	1·395 (15)
C(6)–N(3)	1·324 (2)	1·321 (4)	1·317 (8)
C(4)–H(4)	1·082 (5)	–	
C(5)–H(5)	1·084 (5)	–	
C(6)–H(6)	1·081 (5)	–	
N(4)–H(8)	1·018 (5)	–	

* Neutron diffraction data.
† X-ray diffraction data.

This neutron study makes it possible to distinguish unambiguously carbon and nitrogen atoms of the pyrazole rings and thus to establish that these rings are coordinated to the transition metal *via* a nitrogen atom. The hydrogen atom positions were accurately determined in this experiment. There are six (C–H) distances and two (N–H) distances. For the two crystallographically independent pyrazole rings the average N–H distance of 1·02 Å is significantly shorter than the average C–H distance of 1·08 Å. In the complex $Co(Im)_6(NO_3)_2$ (Im = imidazole = NHCH:NCH:CH), also studied by neutron diffraction (Prince, Mighell, Reimann & Santoro, 1972), a similar difference in N–H and C–H bond lengths is observed.

The accurate location of the hydrogen atoms established that there is internal hydrogen bonding in the complex similar to that postulated in the related nickel complexes. These bonds are presumed to be responsible for the fact that the plane of each pyrazole ring and the plane defined by the coordinating pyrazole nitrogen atoms N(1), N(1′), N(3), and N(3′) form a dihedral angle of about 90°. The N–H···Cl hydrogen bonds are stronger than the C–H···Cl bonds since the hydrogen atoms attached to the nitrogen atoms N(2) and N(4) are closer to the chlorine

Table 6. *Comparison of the bond angles of the pyrazole rings in* $Cu(Pz)_4Cl_2$, $Ni(Pz)_4Cl_2$ *and* $Ni(Pz)_4Br_2$ *given respectively, in columns one, two and three*

	Ring 1				Ring 2		
C(3)–N(1)–N(2)	107·2	106·2	105·5	N(4)–N(3)–C(6)	106·2	104·9	104·3
N(1)–N(2)–C(1)	110·8	111·1	112·3	C(4)–N(4)–N(3)	111·3	111·7	111·8
N(2)–C(1)–C(2)	107·1	106·6	104·8	C(5)–C(4)–N(4)	107·3	107·4	107·4
C(1)–C(2)–C(3)	105·4	105·8	107·5	C(6)–C(5)–C(4)	104·6	104·8	104·8
C(2)–C(3)–N(1)	109·6	110·3	110·0	N(3)–C(6)–C(5)	110·6	111·1	111·7

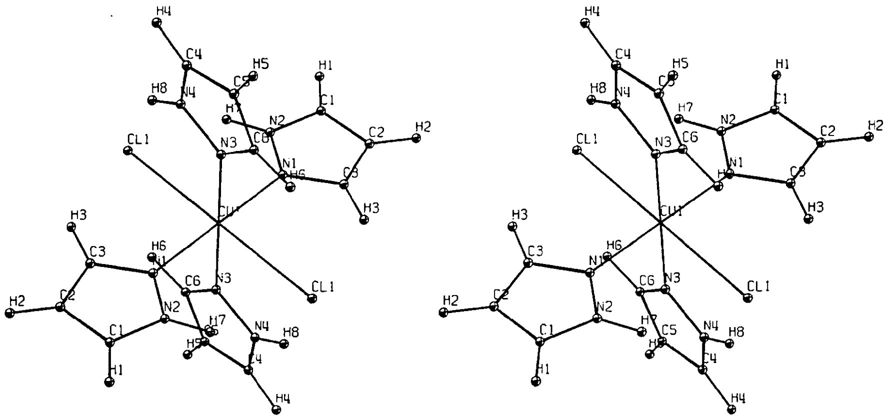

Fig. 1. Stereoscopic view of the complex dichlorotetrapyrazolecopper(II), $Cu(Pz)_4Cl_2$. For simplicity the atoms are drawn as spheres of arbitrary size.

atoms than the hydrogen atoms attached to C(3) and C(6). The distances for these four internal hydrogen bonds are: in ring one, N(2)–H(7)···Cl 2·40 Å and C(3)–H(3)···Cl 2·66 Å; in ring two, N(4)–H(8)···Cl 2·28 Å and C(6)–H(6)···Cl 2·73 Å. As the N–H···Cl bonds are stronger than the C–H···Cl bonds, the rings are tipped slightly toward the chlorine atoms forming the N–H···Cl bonds, as shown in Table 7. Both the ring tipping and the shorter hydrogen-bond distance involving H(8) show that ring 2 is more strongly hydrogen bonded than ring 1.

Table 7. *Tilt of the pyrazole rings due to hydrogen bonding in* $Cu(Pz)_4Cl_2$, $Ni(Pz)_4Cl_2$ *and* $Ni(Pz)_4Br_2$

Angle	$Cu(Pz)_4Cl_2$	$Ni(Pz)_4Br_2$	$Ni(Pz)_4Cl_2$
Ring 1			
N(2)–N(1)–Cu	125°	126°	123°
C(3)–N(1)–Cu	128	128	130
Ring 2			
N(4)–N(3)–Cu	122	122	121
C(6)–N(3)–Cu	132	134	134

The data of Table 7 show that a similar tipped ring orientation is found in the complexes $Ni(Pz)_4Cl_2$ and $Ni(Pz)_4Br_2$.

Although the molecular structure of $Cu(Pz)_4Cl_2$ is very similar to those of $Ni(Pz)_4Cl_2$ and $Ni(Pz)_4Br_2$, the packing of the copper complex is different from that of the nickel complexes. If one were to reverse the assignment of N(2) and C(3) in ring 1 in the copper complex (equivalent to a rotation of 180° about the N(1)–Cu bond or, alternatively, to a rotation of 90° about the Cu–Cl bond), then the packing of the three compounds would be the same. There is the possibility that the assignment of N(2) and C(3) for the nickel complexes was incorrect as the structures of these compounds were determined by X-ray diffraction. For this reason a neutron structure determination of $Ni(Pz)_4Cl_2$ is planned. However, the evidence available at present (*i.e.*, the close agreement of bond distances and angles of the Pz ligands, of the hydrogen bonding and of the thermal parameters for the three complexes, and the fact that the *R* values are higher if one refines the nickel compounds with the N(2) and C(3) atoms interchanged) strongly suggests that the assignment of N(2) and C(3) is correct as reported.

All computer calculations (except for the final refinement cycles) on this structure were performed using the X-RAY Program System (1972).

The stereo figure was drawn with the *ORTEP* Fortran plot program (Johnson, 1965).

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Structure Cristalline du Tripolyphosphate de Zinc Heptadécahydraté: $Zn_5(P_3O_{10})_2.17H_2O$

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Zinc tripolyphosphate heptadecahydrate, $Zn_5(P_3O_{10})_2.17H_2O$, is triclinic with $a = 10{\cdot}766$ (8), $b = 10{\cdot}316$ (8), $c = 8{\cdot}525$ (5) Å, $\alpha = 111{\cdot}39$ (5), $\beta = 115{\cdot}08$ (5), $\gamma = 70{\cdot}19$ (5)°, and $Z = 1$. The atomic arrangement has been determined by using 3558 independent reflexions. The final *R* value is 0·04. This is the first known crystal structure of a bivalent cation tripolyphosphate.

Introduction

Les principales caractéristiques cristallographiques et la préparation chimique du tripolyphosphate de zinc heptadécahydraté: $Zn_5(P_3O_{10})_2.17H_2O$ ont déjà été décrites (Averbuch-Pouchot & Durif, 1975). Nous rappelons simplement sa maille: $a = 10{,}766$ (8), $b = 10{,}316$ (8), $c = 8{,}525$ (5) Å; $\alpha = 111{,}39$ (5), $\beta =$