

Short Communications

Crystal structure of bis(3,5-dimethyl-1-guanyl pyrazole) copper(II) nitrate

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Crystal structure / Pyrazole derivative

Abstract. The title compound $\text{Cu}(\text{C}_6\text{N}_4\text{H}_{10})_2(\text{NO}_3)_2$ crystallizes in space group $P\bar{1}$ with $a = 9.708(3)$, $b = 5.464(2)$, $c = 9.367(3)$ Å, $\alpha = 92.99(3)$, $\beta = 101.24(3)$ and $\gamma = 108.54(3)^\circ$, $Z = 1$, $\rho_c = 1.66$ gm/cm³, $\mu = 2.05$ mm⁻¹. The structure was solved by heavy-atom technique and was refined by least-squares method to $R = 0.056$. The Cu atom on the centre of inversion displayed a distorted octahedral coordination.

Introduction

Substituted pyrazoles have long been acclaimed for their medicinal values (Elderfield, 1959). The study of pyrazole compounds with metal ions is of interest as the ligand is closely related to biological systems. The crystal structure analysis of the title compound has been undertaken in order to study the coordination behaviour of pyrazole with transition metal ions.

Experimental

3,5-dimethyl-1-guanyl pyrazole nitrate solution was prepared by refluxing an equimolar mixture of aminoguanidine nitrate and freshly distilled acetylacetone in aqueous ethanol. The title complex salt was synthesized

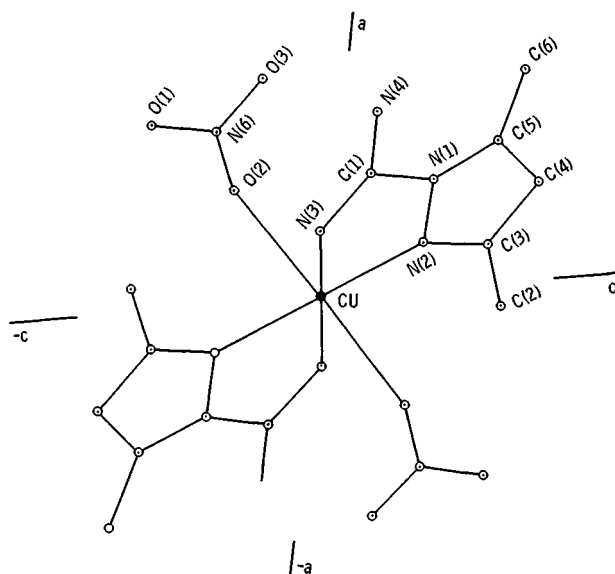


Fig. 1. Environment around Cu atom looking down *c* axis

by mixing this aqueous ethanolic solution with Cu(II) nitrate trihydrate in 2:1 molar proportion and on heating on a steam bath. A microcrystalline blue compound separated out. Recrystallization was done from alcohol when long plate-like crystals were obtained. Space group and approximate cell dimensions were obtained from rotation and Weissenberg photographs and later were more accurately determined on a diffractometer centering 15 reflections in the range $40^\circ < 2\theta < 67^\circ$. A crystal of dimension $0.25 \times 0.20 \times 0.30$ mm was used for data collection on a SYNTEX P1 diffractometer with graphite monochromatized $\text{CuK}\alpha$ radiation. Three standard reflections, measured after 97 reflections, showed no significant change in intensity. The data were corrected for geometrical factors.

Structure determination and refinement

A Patterson map was calculated which showed no metal-metal peak in the general position. Since there is only one formula unit per unit cell, Cu can be placed at the origin of the centrosymmetric cell. A Fourier synthesis at this stage revealed all the non-hydrogen atoms. The structure was refined by block-diagonal least-squares calculation by minimization of $\sum W(|F_o| - |F_c|)^2$ where $W = 1/\sigma^2$. Hydrogen atoms were located from a difference Fourier map and the positional and thermal parameters of hydrogen atoms were kept fixed in all refinements. Refinement was continued until all the atomic parameter shift were smaller than their standard deviations. The

Table 1. Atomic coordinates of non-hydrogen atoms ($\times 10^4$) and hydrogen atoms ($\times 10^3$) and thermal parameters (\AA^2). $B_{eq} = 4/3 \sum_{i,j} \beta_{ij} (\tilde{a}_i \cdot \tilde{a}_j)$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B_{eq}/B_{iso}^*
Cu	0	0	0	2.97
N(1)	-2077(4)	-22(8)	1770(4)	2.09
N(2)	-888(4)	-881(9)	1773(4)	1.97
N(3)	-1380(5)	1952(9)	-181(4)	2.23
N(4)	-3337(5)	2688(9)	655(5)	2.78
N(5)	-3291(5)	-3382(9)	-2187(5)	2.94
C(1)	-2284(6)	1614(10)	683(5)	1.99
C(2)	476(7)	-3214(12)	3367(6)	3.55
C(3)	-735(6)	-2054(10)	2967(5)	2.21
C(4)	-1840(6)	-2010(11)	3721(6)	2.74
C(5)	-2674(6)	-696(11)	2943(5)	2.24
C(6)	-3976(7)	-97(13)	3301(7)	3.65
O(1)	-3506(6)	-2483(12)	-3346(5)	6.70
O(2)	-2097(5)	-3796(8)	-1727(5)	3.86
O(3)	-4213(5)	-3825(9)	-1418(5)	4.23
H1C(2)	599	-318	430	2.55*
H2C(2)	131	-200	312	2.55*
H3C(2)	10	-422	258	2.55*
H(C4)	-197	-229	457	2.10*
HN(3)	-160	262	-101	1.79*
HN(4)	-380	259	121	2.18*
H1(C6)	-361	168	360	2.82*
H2(C6)	-432	-90	402	2.82*
H3(C6)	-493	-67	252	2.82*

Table 2. Bond lengths (\AA) and angles (0°) with their e.s.d.'s

Cu—N(2)	2.028(4)	N(2)—Cu—N(3)	101.0(2)
Cu—N(3)	1.950(4)	N(2)—Cu—O(2)	93.1(2)
N(1)—N(2)	1.376(3)	N(3)—Cu—O(2)	92.0(2)
N(2)—C(3)	1.325(6)	N(3)—C(1)—N(1)	114.9(2)
C(3)—C(2)	1.501(8)	N(3)—C(1)—N(4)	126.0(5)
C(3)—C(4)	1.400(7)	N(1)—N(2)—C(3)	106.1(3)
C(4)—C(5)	1.378(8)	N(2)—C(3)—C(4)	109.9(5)
C(5)—C(6)	1.497(4)	C(3)—C(4)—C(5)	106.8(3)
C(5)—N(1)	1.354(5)	C(4)—C(5)—N(1)	106.4(4)
N(1)—C(1)	1.416(7)	O(2)—N(5)—O(1)	120.6(5)
C(1)—N(4)	1.330(6)	O(1)—N(5)—O(3)	121.4(5)
C(1)—N(3)	1.284(7)	O(1)—N(5)—O(2)	120.6(5)
N(5)—O(1)	1.223(7)		
N(5)—O(2)	1.250(6)		
N(5)—O(3)	1.229(7)		

final R value converged to 0.056. The final difference Fourier map was featureless. The scattering factors of the atoms were taken from International Tables for X-ray Crystallography (1974).

Discussion

The Cu atom of the bidentate metal complex is located at the centre of inversion and is surrounded by four nitrogen atoms of two centrosymmetrically related pyrazole groups in a square plane with $\text{Cu}-\text{N}(2) = 2.028(4)$, $\text{Cu}-\text{N}(3) = 1.950(4)$ Å. In this complex the tertiary nitrogen atom of the ring is the coordination site which has been found in similar other metal complexes with pyrazole (Reiman et al., 1970). The oxygen atoms of the two centrosymmetrically related nitrate moieties complete the coordination around Cu atom to form an elongated octahedron with $\text{Cu}-\text{O} = 2.597(5)$ Å. The pyrazole ring is almost planar with a maximum deviation of $0.013(4)$ Å from the least-squares plane. The equatorial arrangement around the Cu atom is also planar and the dihedral angle between this plane and the plane of the pyrazole ring is 9.5° . The crystal structure is stabilized by hydrogen bonding network. All the hydrogen atoms attached to N(2) and N(4) are involved in intermolecular hydrogen bonding with the oxygen atoms of the neighbouring nitrate groups.

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