Synthesis, Magnetic Properties, and *X*-Ray Structure of *catena*-μ_3-Nitrato-*O,O′,O″*-[μ_3-hydroxo-1-nitrato-1,2;1,3;2,3-tris(μ-pyrazolato-*N,N′*)-2,3-bis(pyrazole-*N*^{2})tricopper(II) Monohydrate].† An Unusual Chain of Trinuclear Copper Clusters

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An unusual trimeric Cu^{II} species of formula $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$ (Hpz = pyrazole) has been prepared from air oxidation of $[Cu(Hpz)_2(NO_3)]$ in the presence of moisture. The *X*-ray structure of the oxidation product has been determined by single-crystal diffractometer techniques, and has been compared with a few related structures, all containing the pyramidal trimeric unit $Cu_3(OH)$. The compound crystallizes in the space group $P2_1$ with $a = 7.756(2)$, $b = 17.639(3)$, $c = 8.883(1)$ Å, $\beta = 91.18(1)°$, and $Z = 2$. The intensities of 3 640 independent reflections were used to determine the structure. The structure was solved and refined using standard heavy-atom and least-squares techniques to a residual *R* value of 0.0241 for 3 128 reflections with $I > 2\sigma(I)$. The structure consists of trimeric units $Cu_3(OH)(pz)_3$ containing an almost flat Cu_3N_6 ring and a pyramidal Cu_3O group with Cu–O distances of 1.994 Å and an (averaged) Cu–O–Cu angle of 114°. Each copper is co-ordinated by four ligands in an almost square planar manner with two nitrogens from the bridging pyrazolato-groups and one oxygen from the bridging OH group. The fourth equatorial ligand is either the N-atom of a neutral pyrazole (for two Cu atoms) or the oxygen of a unidentate co-ordinating nitrato-ligand (for the third Cu atom). The fifth axial ligand for each copper ion is another nitrato-group. This nitrato-group links trimers together in chains, with two oxygens bound to coppers of one trimer, and the third oxygen binding to the third copper of the neighbouring trimer, resulting in chains of $-O_2NO-CuCu_2O_2NO-CuCu_2-O_2-$. The dominant magnetic exchange in the structure occurs within each trimer, resulting in a compound having only one unpaired spin per three copper ions. An additional magnetic exchange interaction occurs between the trimers, using the nitrate-bridged chain. This interaction is only evident at very low temperatures. Due to the occurrence of rapid spin-lattice relaxation no e.s.r. spectra can be obtained at ambient temperatures, but instead n.m.r. spectra have been recorded.

Dimeric hydroxo-bridged copper(II) compounds form a large class of magnetically interesting compounds.[1-3] Usually these compounds have the stoicheiometry $[L_nCu(OH)_2CuL_n][anion]_2$ (L = ligand), with square planar or tetragonal co-ordination geometries for the metal ions. Hatfield and co-workers [4] have pointed out an interesting correlation which exists between the sign and magnitude of the magnetic exchange interaction (usually expressed as $2J$) and the angle Cu–O–Cu (usually denoted as θ). For values of θ below 97° the exchange appears to be ferromagnetic, whereas for larger values antiferromagnetic exchange occurs. Up to now a linear correlation has been found for $2J$ values between -600 cm^{-1} ($\theta = 105°$) and 150 cm^{-1} ($\theta = 95.5$). When the co-ordination spheres around the copper ions are not coplanar, the $2J$ values are usually smaller, and Kahn and co-workers [5] have indicated how corrections have to be made for these 'roof-shaped' hydroxo-bridged dimers. Copper dimers having a single OH group as a bridging ligand have also been recently reported,[6,7] and in one case also confirmed by an *X*-ray structure analysis.[7] The value of the magnetic exchange appears to be less negative than would be expected from the value of θ for a dihydroxo-bridged dimer. All these copper dimers are usually prepared by adding OH$^-$ to a solution of Cu^{II} in the presence of the appropriate ligand. In many cases the same compounds are also formed by air oxidation of Cu^{I} compounds [3,8] in the presence of the appropriate ligand, the most well known example being the dimeric compounds $[(tmen)Cu(OH)_2Cu(tmen)]^{2+}$ (tmen = *NNN′N′*-tetramethylethylenediamine) which are used as catalysts for the oxidative coupling reactions of phenoles.[9]

In attempts to prepare dihydroxo-bridged copper compounds by air oxidation of $[Cu(Hpz)_2(NO_3)]$ (Hpz = pyrazole) an unexpected product, analysing as $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$, was formed. This paper deals with the synthesis, characterisation, magnetism, and crystal structure of this unusual compound.

Experimental

Starting Materials.—Solvents, pyrazole (Hpz), copper turnings, and $[Cu(H_2O)_6(NO_3)_2]$ were used as commercially available products. The complex $[Cu(Hpz)_4(NO_3)_2]$ was prepared as described earlier [10] and isolated as a deep blue product and $[Cu(Hpz)_2(NO_3)]$ was prepared using a modification of the procedure described before.[11] A suspension of $[Cu(Hpz)_4(NO_3)_2]$ in sodium-dried diethyl ether was stirred with copper turnings until all the solid had turned white. The excess copper turnings were separated from the white powder by decantation in a glove-box system under nitrogen. The white product analysed as $[Cu(Hpz)_2(NO_3)]$ (Cu, C, H, N) and was further characterised by its i.r. spectrum.

Preparation of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$ *and Crystal Growth.*—A sample of $[Cu(Hpz)_2(NO_3)]$ (*ca.* 1 g) was oxidised upon standing in moist air. After 1 d the blue powder

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† *Supplementary data available* (No. SUP 23472, 16 pp.): structure factors, thermal parameters, hydrogen parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m^2.

Table 1. Crystal and diffraction data for $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$

M	692.08
Space group	$P2_1$
Crystal system	Monoclinic
a/Å	7.756(2)
b/Å	17.639(3)
c/Å	8.883(1)
β/°	91.18(1)
U/Å^3	1 215
Z	2
D_m/Mg m^{-3}	1.86(1)
D_c/Mg m^{-3}	1.87
F(000)	339.85
Crystal dimensions/mm	0.5 × 0.3 × 0.3
θ range/°	2—30
Measured reflections	6 397
Independent reflections	3 640
Significant reflections ($I > 2\sigma$)	3 128
Final R (R')	0.0241 (0.0242)
μ/cm^{-1}	26.5
Transmission range (azimuth scan)	0.96—1.04
Diffractometer	CAD-4
Radiation (λ)	Mo-K_α (0.71073 Å)
Monochromator	graphite

was extracted for 1 h with boiling dioxan and filtered off. The resulting blue product was dissolved in boiling ethanol and refluxed for 45 min. A small insoluble fraction was removed by filtration. The filtrate was reduced in volume by vacuum evaporation. Upon standing deep blue crystals separated which could be isolated by filtration, yield 0.45 g (40%) (Found: C, 26.10; H, 2.95; Cu, 27.75; N, 24.35; O, 18.4. Calc. for $C_{15}H_{20}Cu_3N_{12}O_8$: C, 26.20; H, 2.90; Cu, 27.75; N, 24.45; O, 18.65%). The product was also characterised by spectroscopic measurements. A crystal of *ca.* 0.3 × 0.3 × 0.5 mm was isolated for the *X*-ray structure determination.

Physical Methods.—Infrared spectra of the solid compounds were recorded on a Perkin-Elmer 580 spectrophotometer in KBr pellets and in Nujol mulls (4 000—250 cm^{-1}). Electronic spectra (25 000—5 000 cm^{-1}) were obtained on a Beckman DK-2A spectrophotometer fitted with a diffuse reflectance unit. E.s.r. spectra were obtained at *X*-band frequency on a Varian E-3 instrument at temperatures of 300, 77, and 10 K. Proton n.m.r. spectra were obtained using a JEOL-PS 100 spectrometer operating at 100 MHz. Magnetic susceptibility studies in the region 2—300 K were performed using a Faraday balance (80—300 K) and a PAR vibrating sample magnetometer (2—90 K). Elemental analyses were performed by Dr. Pascher, Bonn, Germany and at the University of Technology, Eindhoven, The Netherlands.

X-*Ray Methods and Structure Determination.*—The structural investigation commenced with a crystal of a limited quality, showing many split diffraction peaks. However it was possible to define a mosaic vector from which values of ψ could be calculated for use in obtaining setting angles with minimum set up.

The diffraction data thus obtained were used after corrections for Lorentz, polarisation, and absorption effects. After location of the copper atoms in a Patterson map the non-hydrogen atoms were obtained by standard Fourier techniques. The hydrogen atoms were placed on calculated positions (C–H = 1.0 Å) and non-hydrogen atoms were refined anisotropically. The refinement converged at $R = 0.14$ for 1 971 observed reflections. The hydrogen bonding plays an important role in the structure, but it could not be determined with sufficient accuracy from the available data. Furthermore, it could not be determined whether an O atom, an OH group, or a H_2O group formed the bridge between the three copper atoms.

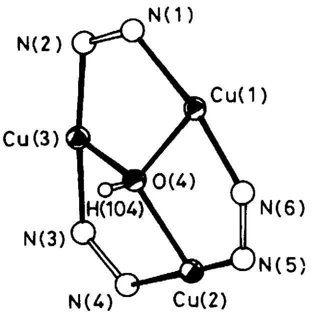

Figure 1. ORTEP drawing of the trinuclear unit in $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$. Only the nine-membered ring Cu_3N_6 is shown with the bridging OH group as the top of the pyramid $Cu_3(OH)$

Because of the interesting magnetic properties of the compound it was decided to search for better crystals. After many trials (see above) a batch of high quality crystals was obtained from which a suitable crystal with a bar shape was used to obtain a new data set. The relevant data of this crystal and the instrumental information are summarised in Table 1.

Precise lattice constants and the space group were determined from a least-squares refinement of the angular settings of 24 reflections with $5 < \theta < 15$. The cell parameters for the two crystals appeared the same within experimental error. For the refinement of the structure the atomic positions of all non-hydrogen atoms, obtained from the first crystal, were used. After a few cycles of least-squares refinements, using anisotropic thermal parameters for all non-hydrogen atoms, all except one hydrogen could be located in a difference-Fourier map. Positions and B values were refined for a few cycles; H(11) was calculated at a C–H distance of 0.95 Å. In all refinement stages unit weights were used.

A final difference-Fourier synthesis showed no residual electron density. The final values for the residuals were $R = 0.0241$ and $R' = 0.0242$ for those 3 128 reflections with $I > 2\sigma(I)$. Atomic scattering factors for neutral atoms were taken from ref. 12 and where appropriate used with correction for the anomalous scattering. Because of the expected small effect upon the transmissions ($\mu_{calc.} = 26.5$cm^{-1}, resulting in transmission factors between 0.41 and0.47) no absorption correction was applied.

Positional parameters are given in Table 2. The initial structure determination and refinement was carried out using a local Eclipse S/230 mini-computer with a locally adapted version of the SHELX 76 package (named ILIAS). The final structure determination was carried out with IBM and Amdahl computers using a locally available set of programs for refinement. Drawings were produced using the ORTEP program.

Results and Discussion

Description of the Crystal Structure.—The structure of the title compound consists of trimeric units, $Cu_3(OH)(pz)_3$. The geometry of such a trimeric unit (excluding the pyrazole carbon atoms) is depicted in Figure 1. The nine-membered ring Cu_3N_6 is almost planar, as seen from the deviations of the N atoms to the plane through the three Cu atoms, which

Table 2. Positional parameters ($\times$ 10^4) of the non-hydrogen atoms of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Cu(1)	3 045.4(6)	1 035.9(3)	−847.6(5)	C(5)	−78(6)	4 131(3)	−4 308(5)
Cu(2)	2 850.3(6)	2 159.9(3)	−3 850.8(5)	C(6)	1 104(6)	3 625(3)	−4 831(5)
Cu(3)	283.3(6)	2 507.3(3)	−922.7(6)	C(7)	4 980(7)	889(3)	−5 019(4)
N(1)	1 610(4)	1 274(2)	873(4)	C(8)	5 615(7)	199(3)	−4 541(6)
N(2)	460(4)	1 859(2)	818(4)	C(9)	5 063(6)	136(3)	−3 076(6)
N(3)	322(4)	3 195(2)	−2 653(4)	C(10)	4 577(6)	−349(3)	764(5)
N(4)	1 343(4)	3 060(2)	−3 837(4)	C(11)	6 142(7)	−566(3)	1 434(6)
N(5)	4 074(4)	1 217(2)	−3 927(4)	C(12)	7 135(7)	63(3)	1 380(8)
N(6)	4 124(4)	749(2)	−2 716(4)	C(13)	4 067(6)	2 673(3)	−6 979(5)
N(7)	4 636(4)	368(2)	343(4)	C(14)	5 388(7)	3 093(3)	−7 591(5)
N(8)	6 229(5)	611(2)	726(5)	C(15)	6 436(7)	3 278(3)	−6 422(6)
N(9)	4 287(4)	2 612(2)	−5 496(4)	O(1)	−2 632(5)	1 997(3)	−1 601(7)
N(10)	5 747(5)	2 990(2)	−5 173(4)	O(2)	−4 897(6)	2 034(2)	−347(4)
N(11)	−180(5)	3 798(2)	920(4)	O(3)	−4 635(7)	2 787(3)	−2 150(3)
N(16)	−4 015(4)	2 290(2)	−1 383(4)	O(4)	1 587(3)	1 761(2)	−2 092(3)
C(1)	1 522(5)	952(3)	2 248(5)	O(5)	−1 099(4)	3 306(2)	197(3)
C(2)	301(6)	1 324(3)	3 079(5)	O(6)	1 371(5)	3 696(2)	1 086(5)
C(3)	−322(6)	1 886(3)	2 153(5)	O(7)	−947(6)	4 353(2)	1 441(5)
C(4)	−545(6)	3 840(3)	−2 937(5)	O(10)	552(5)	5 629(2)	−7 033(5)

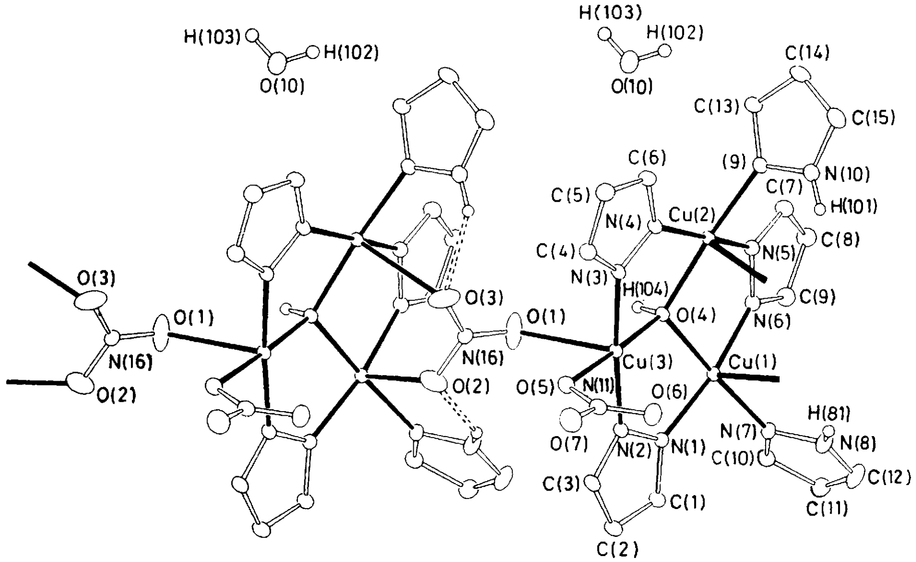

Figure 2. ORTEP drawing of two formula units of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$. The hydrogen atoms attached to the carbon atoms of the pyrazole rings have been omitted for clarity. The water molecules have been shifted along the *c* axis by the symmetry operation $z + 1$

are 0.07, 0.04, 0.12, 0.12, −0.34, and −0.37 Å for N(1)—N(6) respectively. Similar trimeric $Cu_3(OH)$ units have been reported before for a variety of ligands, such as pyridine-2-carbaldehyde oximate (pao),[13] 2-diethylaminoethanol,[14] 3-methyl-3-propylaminobutan-2-one oximate (prbo),[15] ethylsalicylate,[16] and trifluoroacetate.[16] The present compound is the first one with such a simple, symmetric bridging ligand as the pyrazolate (pz) ion.

The trimers are further co-ordinated by two unidentate pyrazole ligands, and one unidentate nitrate ion. One nitrate group forms a bridge between the trimeric units, resulting in a chain along the *c* axis. Part of this chain, together with the atomic numbering, is presented in Figure 2. Relevant bond lengths are presented in Table 3 and bond angles are in Table 4.

The co-ordination geometry around each of the Cu^{II} ions is square pyramidal with Cu–N and Cu–O(equatorial) bond lengths which are normal for Cu^{II} in this geometry. The Cu–O(axial) bond lengths vary from 2.412(4) Å for Cu(1)–O(2) to 2.496(4) Å for Cu(3)–O(1), to 2.681(5) Å for Cu(2)–O(3). The distance Cu(3)–O(6) is not considered to be important in bonding, because of the angle O(5)–Cu(3)–O(6) (49°). The Cu · · · Cu distances within the cluster appear to be somewhat larger than the averaged values reported for the other trinuclear copper clusters. Some relevant geometrical information is compared in Table 5. From this Table it is seen that the larger Cu · · · Cu distance in our compound is further reflected by the relatively large Cu–O(4)–Cu angles and the distance of the O(4) atoms to the plane of the three Cu atoms. The origin of the larger Cu distance in our compound could be the difference in the bridging organic ligand, which is the pyrazolate anion in our compound and which is the NO unit of the oximato-group of the other compounds

Table 3. Relevant bond lengths (Å) in $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$

Cu(1)-Cu(2)	3.324 7(7)	N(3)-N(4)	1.350(4)	O(4)-O(10)	2.700(5)
Cu(2)-Cu(3)	3.364 3(6)	N(3)-C(4)	1.343(5)	O(2)-N(8)	2.818(6)
Cu(1)-Cu(3)	3.365 2(7)	C(4)-C(5)	1.377(6)	O(3)-N(10)	2.732(6)
Cu(1)-O(4)	2.022(3)	C(5)-C(6)	1.368(7)	O(10)-O(7)	2.863(6)
Cu(2)-O(4)	1.990(3)	C(6)-N(4)	1.341(5)	O(4)-H(104)	0.83(6)
Cu(3)-O(4)	1.969(3)	N(5)-N(6)	1.356(5)	C(1)-H(1)	0.94(5)
Cu(1)-N(1)	1.955(3)	N(5)-C(7)	1.341(6)	C(2)-H(2)	1.02(6)
Cu(1)-N(6)	1.941(3)	C(7)-C(8)	1.376(7)	C(3)-H(3)	0.75(5)
Cu(1)-N(7)	1.993(4)	C(8)-C(9)	1.383(7)	C(4)-H(4)	0.89(5)
Cu(1)-O(2)	2.412(4)	C(9)-N(6)	1.345(6)	C(5)-H(5)	0.89(5)
Cu(2)-N(4)	1.972(3)	N(7)-N(8)	1.344(5)	C(6)-H(6)	0.87(5)
Cu(2)-N(5)	1.917(4)	N(7)-C(10)	1.320(6)	C(7)-H(7)	0.82(7)
Cu(2)-N(9)	2.020(3)	C(10)-C(11)	1.395(7)	C(8)-H(8)	1.04(5)
Cu(2)-O(3)	2.681(5)	C(11)-C(12)	1.351(9)	C(9)-H(9)	0.94(5)
Cu(3)-N(2)	1.926(3)	C(12)-N(8)	1.322(7)	C(10)-H(10)	0.88(4)
Cu(3)-N(3)	1.959(3)	N(9)-N(10)	1.340(5)	C(12)-H(12)	0.71(7)
Cu(3)-O(1)	2.496(4)	N(9)-C(13)	1.330(5)	N(8)-H(81)	0.79(6)
Cu(3)-O(5)	2.042(3)	C(13)-C(14)	1.384(6)	C(13)-H(13)	1.01(5)
Cu(3)-O(6)	2.869(4)	C(14)-C(15)	1.346(8)	C(14)-H(14)	0.98(5)
N(1)-N(2)	1.365(5)	C(15)-N(10)	1.342(6)	C(15)-H(15)	0.92(7)
N(1)-C(1)	1.350(5)	N(11)-O(5)	1.287(5)	N(10)-H(101)	0.83(5)
C(1)-C(2)	1.378(6)	N(11)-O(6)	1.223(5)	O(10)-H(104)	1.87(6)
C(2)-C(3)	1.370(7)	N(11)-O(7)	1.239(5)	O(10)-H(102)	0.81(8)
C(3)-N(2)	1.343(5)	N(16)-O(1)	1.210(5)	O(10)-H(103)	0.80(8)
		N(16)-O(2)	1.243(5)	O(3)-H(101)	1.99(5)
		N(16)-O(3)	1.204(5)	O(2)-H(81)	2.16(6)
				C(11)-H(11)	1.0

Table 4. Relevant bond angles (°) in $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$

Cu(1)-O(4)-H(104)	95(4)	Cu(3)-O(4)-Cu(1)	115.0(1)	N(9)-C(13)-C(14)	110.6(4)
Cu(2)-O(4)-H(104)	109(4)	Cu(2)-O(4)-Cu(3)	116.4(1)	C(13)-C(14)-C(15)	105.5(4)
Cu(3)-O(4)-H(104)	108(4)	Cu(2)-O(4)-Cu(1)	112.0(1)	C(14)-C(15)-N(10)	107.6(4)
N(1)-Cu(1)-N(7)	93.7(1)			C(15)-N(10)-N(9)	111.1(4)
N(6)-Cu(1)-N(7)	91.5(1)	N(2)-Cu(3)-O(4)	89.9(1)	N(10)-N(9)-C(13)	105.2(3)
N(6)-Cu(1)-O(4)	86.8(1)	N(3)-Cu(3)-O(4)	89.1(1)	N(1)-C(1)-C(2)	109.5(4)
N(1)-Cu(1)-O(4)	88.3(1)	N(2)-Cu(3)-O(5)	92.7(1)	C(1)-C(2)-C(3)	105.0(4)
N(1)-Cu(1)-O(2)	94.8(1)	N(3)-Cu(3)-O(5)	88.4(1)	C(2)-C(3)-N(2)	110.2(4)
N(7)-Cu(1)-O(2)	86.2(2)	O(1)-Cu(3)-O(4)	96.0(1)	C(3)-N(2)-N(1)	107.5(3)
N(6)-Cu(1)-O(2)	93.1(1)	O(1)-Cu(3)-O(5)	83.4(1)	N(2)-N(1)-C(1)	107.8(3)
O(2)-Cu(1)-O(4)	60.14(8)	N(2)-Cu(3)-O(1)	91.7(2)		
N(1)-Cu(1)-N(6)	170.7(1)	N(3)-Cu(3)-O(1)	93.6(2)	N(3)-C(4)-C(5)	110.0(4)
O(4)-Cu(1)-N(7)	175.7(1)	Cu(3)-O(5)-N(11)	114.7(3)	C(4)-C(5)-C(6)	104.3(4)
N(4)-Cu(2)-N(9)	91.3(1)	O(5)-N(11)-O(7)	117.0(4)	C(5)-C(6)-N(4)	110.2(4)
N(5)-Cu(2)-N(9)	92.1(1)	O(7)-N(11)-O(6)	123.4(4)	C(6)-N(4)-N(3)	107.9(3)
N(5)-Cu(2)-O(4)	88.5(1)	O(6)-N(11)-O(5)	119.7(4)	N(4)-N(3)-C(4)	107.6(3)
N(4)-Cu(2)-O(4)	88.7(1)			N(5)-C(7)-C(8)	110.4(4)
N(4)-Cu(2)-O(3)	95.1(1)	N(16)-O(1)-Cu(3)	127.5(3)	C(7)-C(8)-C(9)	104.3(4)
N(5)-Cu(2)-O(3)	91.3(1)	N(16)-O(2)-Cu(1)	110.9(3)	C(8)-C(9)-N(6)	109.8(4)
N(9)-Cu(2)-O(3)	80.8(1)	N(16)-O(3)-Cu(2)	107.3(3)	C(9)-N(6)-N(5)	107.9(3)
O(3)-Cu(2)-O(4)	89.86(8)	O(3)-N(16)-O(1)	124.5(5)	N(6)-N(5)-C(7)	107.7(4)
N(9)-Cu(2)-O(4)	170.6(1)	O(2)-N(16)-O(1)	117.8(5)		
N(4)-Cu(2)-N(5)	173.2(1)	O(2)-N(16)-O(3)	117.6(5)	N(7)-C(10)-C(11)	110.4(4)
O(5)-Cu(3)-O(6)	49.0(1)	H(81)-N(8)-C(12)	135(4)	C(10)-C(11)-C(12)	104.6(4)
N(2)-Cu(3)-O(6)	85.4(1)	N(8)-H(81)-O(2)	163(4)	C(11)-C(12)-N(8)	108.5(5)
N(3)-Cu(3)-O(6)	91.5(1)	N(10)-H(101)-O(3)	124(4)	C(12)-N(8)-N(7)	110.9(4)
N(2)-Cu(3)-N(3)	174.7(1)	Cu(1)-O(2)-H(81)	77(1)	N(8)-N(7)-C(10)	105.7(4)
O(4)-Cu(3)-O(5)	177.3(1)	Cu(2)-O(3)-H(101)	76(1)		
		N(7)-N(8)-H(81)	114(3)	H(103)-O(10)-H(101)	109(8)
		N(9)-N(10)-H(101)	115(3)		

in Table 5. In all these compounds the trimeric clusters are held together by bridging ligands which are equatorial ligands for the Cu^{II} ions. In addition all compounds also have weakly bound axial ligands that also stabilise the trimeric unit. In the compound with pao [13] the sulphate ion bridges in a unique tridentate manner between the three atoms of one unit. In the compound with prbo [14] axially co-ordinated water molecules stabilise the trimer by hydrogen bonding within the lattice. In the compound with 3-phenyliminobutan-2-one oximate (phbo) [15] a perchlorate ion bridges two coppers additionally, whereas in our compound the nitrato-ion uses O(2) and O(3) to bridge two coppers within one trimer to the other trimer [using O(1) as clearly shown in Figure 2].

The crystal lattice of the present compound is further stabilised by a water molecule which is strongly hydrogen

Table 5. Comparison of structural parameters in trinuclear clusters $Cu_3(OH)$ or Cu_3O

Parameter	$Cu_3(OH)(pao)_3(SO_4)$ [a]	$Cu_3(OH)_{0.5}(prbo)_3$ [b]	$Cu_3(OH)(phbo)_3$ [c]	$Cu_3O(dpeo)_3$ [d]	$Cu_3(OH)(pz)_3$
Cu · · · Cu/Å	3.22	3.246	3.19	3.172 3.183 3.177	3.325 3.364 3.365
Cu-O/Å	1.99	1.97	1.946 1.969 1.978	1.854 1.860 1.890	1.969 1.990 2.022
Cu-O-Cu/°	108.2	110.9	107.1 109.3 110.0	115.5 116.5 117.6	112.0 115.0 116.4
O · · · Cu_3 plane/Å	0.697	0.70	0.695	0.352	0.478
Ref.	13	15	26	26 [e]	This work

[a] pao = Pyridine-2-carbaldehyde oximate. [b] prbo = 3-Methyl-3-propylaminobutan-2-one oximate. [c] phbo = 3-Phenyliminobutan-2-one oximate. [d] dpeo = 2-Methylimino-1,2-diphenylethanone oximate. [e] This compound is in fact hexanuclear with Cu · · · Cu distances between the two trimeric sub-units of 3.107—3.415 Å. Two other hexanuclear species have been omitted from this Table (see refs. 14 and 16). The trimeric units in these compounds are much more asymmetric with Cu · · · Cu distances ranging from 2.93 to 3.67 [14] or 3.13 to 3.47 Å.[16]

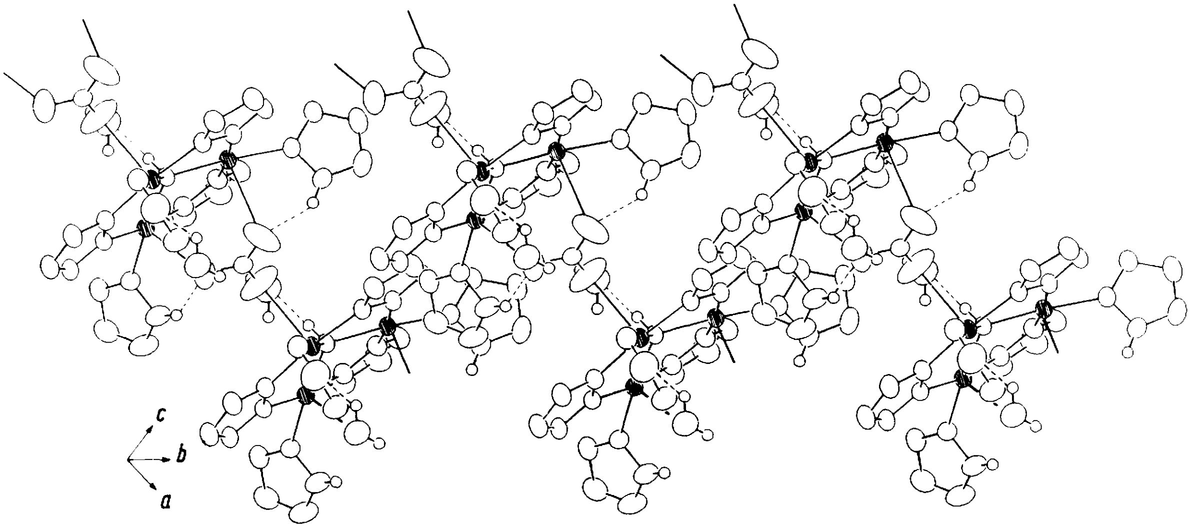

Figure 3. Crystal packing of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$ showing the hydrogen-bond interactions as dashed lines

bonded to the OH group of the trimeric unit $Cu_3(OH)$ with an O(10) · · · O(4) distance of 2.700(5) Å. This hydrogen bond has been omitted from Figure 2 for clarity. The water molecule drawn there is a symmetry related one. The crystal packing of the molecule is depicted in Figure 3 which also shows the intermolecular hydrogen bonds.

At least two of the other trimeric species [13,15] show hydrogen bonding of the H atom of the $Cu_3(OH)$ group with water or with counter ions. Further, significant intratrimer stabilisation occurs by hydrogen bond donation from the pyrazole N-H protons towards the O(2) and O(3) atoms of the bridging nitrate groups, as seen from the distances N(8) · · · O(2) and N(10) · · · O(3), which are 2.818 and 2.732 Å respectively. The protons of the water molecule in the lattice donate hydrogen bonds to O(7) and O(4). The distance to the O(4) atom has been given above; the distance O(10) · · · O(7) is 2.863 Å. The unit $M_3(pz)_3$ forming a nine-membered ring is certainly not unique and has been reported before for M = Au [17] and has been proposed for M = Cu^I and Ag^I.[11]

Finally, it should be mentioned that some of the preparations of the title compound which were carried out in the presence of carbon dioxide showed the same *X*-ray powder pattern, but slightly different elemental analyses and also small differences in the i.r. spectra (see below). It appears that up to 30% of the nitrate groups can indeed be replaced by the HCO_3^- group with retention of the same structure. The sample used for the *X*-ray determination was shown to contain less than 5% of CO_3 by full elemental analyses (see above). This observation is of interest because of the recent findings that carbonate ions can form bridges between two [18–20] or even three [21] Cu^{II} ions.

Spectroscopic and Magnetic Measurements.—The square-pyramidal co-ordination geometry around each copper has been confirmed by the ligand-field spectrum, which shows a maximum at 16.6×10^3 cm^{-1} being typical for Cu^{II} in this geometry with this type of ligand.[22,23] The i.r. spectrum of the compound shows the peaks characteristic for pyrazole and the pyrazolate anion.[11,17] In the 1 250—1 500 cm^{-1} region peaks due to the nitrate anion are found,[24] but clear assignments are difficult, because the two nitrate ions have different co-ordination. In the samples that show significant amounts of (bi)carbonate

Table 6. N.m.r. spectra of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$ obtained in $(CD_3)_2CO$ with and without extra Hpz and Hdmpz [a]

	Assignments					
	pz		Hpz	N-H + H_2O	Extra Hdmpz	
Conditions [b]	H^4 [c]	$H^{3,5}$ [c]	H^4 $H^{3,5}$		H^4 [c]	Methyl protons [c]
0.12 mol dm^{-3}	39.5	32.9	24.9 (br) [d]	3.5		
0.12 mol dm^{-3} + 3 eq. Hpz	39.5	32.9	15.3 (br) [d]	3.5		
0.12 mol dm^{-3} + 8 eq. Hpz	39.5	32.5	11.3 (br) [d]	3.4		
0.11 mol dm^{-3} + 1 eq. Hdmpz [e]	39.0	31.0	23.6 (br) [d]	3.4	27.4	1.3
0.11 mol dm^{-3} + 2 eq. Hdmpz [e]	39.0	30.9	21.2 [d]	3.4	26.2	1.3
0.11 mol dm^{-3} + 4 eq. Hdmpz [e]	38.9	30.9	19.0 [d]	3.4	25.8	1.4
0.11 mol dm^{-3} + 6 eq. Hdmpz [e]	38.9	31.0	17.7 [d]	3.5	24.8	1.4
0.11 mol dm^{-3} + 18 eq. Hdmpz [e]	39.0	30.9	9.4, 10.3	3.5	17.8	1.6
0.11 mol dm^{-3} + 50 eq. Hdmpz [e]	39.1	30.8	8.0, 8.8	3.8	12.0	1.9

[a] Hdmpz = 3,5-Dimethylpyrazole. [b] Concentration of complex and equivalents of added Hpz and Hdmpz per Cu. [c] Proton chemical shifts are reported in p.p.m. downfield from $SiMe_4$. [d] The signals for H^4 and $H^{3,5}$ are not resolved. [e] Taken from a different concentration of the trimer.

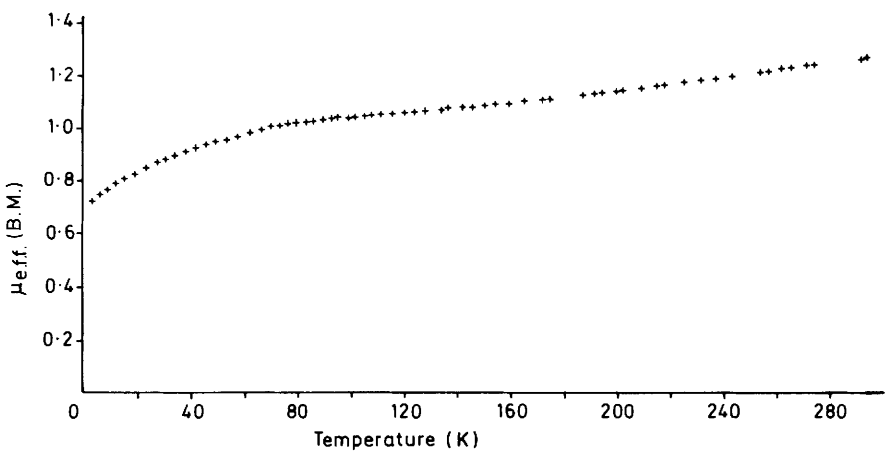

Figure 4. Plot of the magnetic moment of $[Cu_3(OH)(pz)_3(Hpz)_2(NO_3)_2]\cdot H_2O$ as a function of temperature

(see above) some extra peaks in the 1 200—1 500 cm^{-1} region indicate the presence of this ion. In the far-i.r. region some strong peaks occur at 488, 460, and 360 cm^{-1} which can be assigned to either Cu–N(pyrazolate) vibrations or to the $Cu_3(OH)$ group. Weaker bands are found at 323, 298, and 238 cm^{-1} (unassigned). Above 3 000 cm^{-1} three strong peaks occur (3 600, 3 420, and 3 290 cm^{-1}) which are assigned to the ν(O–H) and ν(N–H) stretching vibrations. The values are below those of the free pyrazole ligands and water, due to the relatively strong hydrogen bonding in the lattice (see above).

To investigate the magnetic exchange coupling between the three copper ions, the magnetic susceptibility of the title compound was investigated in the temperature region 2—300 K. As expected, the magnetic moment corresponds roughly with one unpaired electron per trimer (1 B.M. per copper), indicating strong exchange coupling between the metals in the trimer. A plot of the magnetic moment as a function of temperature is given in Figure 4. The values of μ slowly decrease with decreasing temperature. The fact that the μ values decrease below 1 B.M. per copper (or below 1.73 B.M. per trimer) indicates that coupling between different trimers occurs. This should not be expected for a pure trimeric structure and indicates an antiferromagnetically coupled chain of $S = \frac{1}{2}$ species. The coupling between the trimers is much weaker than the intratrimer coupling. The fact that the magnetic moment increases significantly as a function of temperature in the 170—300 K region, suggests that a spin quadruplet state is thermally accessible. In the literature both compounds with and without a thermally accessible quadruplet state have been reported. The origin for the differences has previously been discussed in detail [25,26] in terms of the Cu–O–Cu angles and the nature of the bridging ligand, and will not be repeated here.

The relatively small J (intratrimer) value for our compound (expected to be about -200 cm^{-1}) is in the range predicted by Butcher *et al.*[26]

In an initial attempt to determine g values from e.s.r. spectra, to use in a fit of the magnetic susceptibility data, it was surprisingly found that no room-temperature e.s.r. spectra of this compound could be obtained. Apparently, relaxation phenomena hampered the observation. Only after cooling to below 150 K were weak and broad signals observed, centred around $g = 2.1$. No attempts were undertaken to analyse the details of this spectrum. Because it is well known that paramagnetic systems showing no e.s.r. spectrum may show interesting n.m.r. spectra (and the reverse),[27] we have tried to obtain n.m.r. spectra of the title compound in solution. A solution of *ca.* 10^{-1} mol dm^{-3} in $[^2H_6]$acetone indeed showed signals that could be attributed to protons of pyrazole within the trimeric cluster. To check the assignments, spectra were also recorded after addition of extra pyrazole (and also 3,5-dimethylpyrazole) to the solution. The observed n.m.r. data are summarised in Table 6. From this study it became clear that the unidentate co-ordinated neutral pyrazole molecules are in fast exchange with additional molecules, such as pyrazole and 3,5-dimethylpyrazole, and that the trinuclear cluster remains intact. No further analysis of this exchange process was undertaken.

Conclusions

The present study has shown that interesting polynuclear co-ordination compounds can be obtained upon oxidation of Cu^I pyrazole compounds. The trimeric structure found for the title compound gives rise to a relatively strong magnetic coupling (intratrimer) and a weak intertrimer coupling, the magnitudes of which can be qualitatively understood on the basis of the orientation of the magnetic orbitals of Cu^{II}. Further studies in this area will deal with related systems having substituted pyrazoles and with the use of these compounds as catalysts in oxidation reactions.[28]

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References

1 D. J. Hodgson, *Prog. Inorg. Chem.*, 1975, **19**, 173.
2 V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 1976, **15**, 2107.
3 C. Arcus, K. P. Fivizzani, and S. F. Pavkovic, *J. Inorg. Nucl. Chem.*, 1977, **39**, 285.
4 K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 1973, **9**, 423.
5 M. F. Charlot, S. Jeannin, Y. Jeannin, O. Kahn, J. Lucrece-Abaul, and J. Martin-Frere, *Inorg. Chem.*, 1979, **18**, 1675.
6 M. S. Haddad and D. N. Hendrickson, *Inorg. Chim. Acta*, 1978, **28**, L121.
7 M. S. Haddad, S. R. Wilson, D. J. Hodgson, and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1981, **103**, 384.
8 I. Bodek and G. Davies, *Inorg. Chem.*, 1978, **17**, 1814.
9 A. J. Schouten, G. Challa, and J. Reedijk, *J. Mol. Catal.*, 1980, **9**, 41.
10 J. Reedijk, J. C. A. Windhorst, N. H. M. van Ham, and W. L. Groeneveld, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 234.
11 H. Okkersen, W. L. Groeneveld, and J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1973, **92**, 945.
12 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.
13 R. Beckett and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1972, 291.
14 M. Ahlgren, U. Turpeinen, and K. Smolander, *Acta Crystallogr., Sect. B*, 1980, **36**, 1091.
15 P. F. Ross, R. K. Murmann and E. O. Schlemper, *Acta Crystallogr., Sect. B*, 1974, **30**, 1120.
16 R. J. Butcher, J. W. Overman, and E. Sinn, *J. Am. Chem. Soc.*, 1980, **102**, 3275.
17 G. Minghetti, G. Banditelli, and F. Bonati, *Inorg. Chem.*, 1979, **18**, 658.
18 M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, J. P. Rupich, and K. O. Watkins, *Inorg. Chem.*, 1979, **18**, 2296.
19 M. R. Churchill, G. Davies, M. A. El-Sayed, M. F. El-Shazly, J. P. Hutchinson, and J. P. Rupich, *Inorg. Chem.*, 1980, **19**, 201.
20 M. R. Churchill, G. Davies, M. A. El-Sayed, and J. P. Hutchinson, *Inorg. Chem.*, 1982, **21**, 1002, and refs. therein.
21 G. J. Kolks, S. J. Lippard, and J. V. Waszczak, *J. Am. Chem. Soc.*, 1980, **102**, 4833.
22 B. J. Hathaway, *Coord. Chem. Rev.*, 1981, **35**, 211 and refs. therein.
23 J. Reedijk, *Transition Met. Chem.*, 1981, **6**, 195.
24 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' Wiley, New York, 1978.
25 S. Baral and A. Chakravorty, *Inorg. Chim. Acta*, 1980, **39**, 1.
26 R. J. Butcher, E. J. O'Connor, and E. Sinn, *Inorg. Chem.*, 1981, **20**, 537.
27 G. N. Lamar, W. D. Horrocks, and R. H. Holm, 'NMR of Paramagnetic Molecules, Principles and Applications,' Academic Press, New York, 1973.
28 F. B. Hulsbergen and J. Reedijk, unpublished work.

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