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Copper-Assisted Addition of 3(5)-Methylpyrazole to Acetaldehyde. Synthesis, Structure, and Magnetism of a Unique Tetranuclear Copper(II) Compound: Bis[μ-[1-(1-ethanoyl)-5-methylpyrazolato-N^2,O]]-tetrakis[μ-[3(5)-methylpyrazolato-N^1,N^2]]-bis(nitrato)tetracopper(II)

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The reaction of bis(3(5)-methylpyrazole)copper(I) nitrate with oxygen in the presence of ethanol is shown to yield the tetranuclear species bis[μ-[1-(1-ethanoyl)-5-methylpyrazolato-N^2,O]]-tetrakis[μ-[3(5)-methylpyrazolato-N^1,N^2]]-bis(nitrato)tetracopper(II). In the course of the reaction not only oxidation of the metal but also deprotonation of the 3(5)-methylpyrazole ligand and, most interestingly, addition of part of the so-formed 3(5)-methylpyrazolate to acetaldehyde, present in solution as the result of oxidation of the solvent, occurred. The structure of the tetranuclear compound has been fully determined by single-crystal X-ray analysis and is reported in detail. It crystallizes in the space group $P2_1/n$ with unit cell dimensions a = 11.245 (3) Å, b = 13.690 (4) Å, c = 13.553 (5) Å, β = 109.31 (3)°, and Z = 2. Reflection data up to θ = 25° were collected on an Enraf-Nonius CAD-4 single-crystal diffractometer using graphite-monochromated Mo Kα radiation. The structure was solved with conventional Patterson, Fourier, and least-squares techniques. The final discrepancy index R was 3.1%, based on 2124 observed reflections ($I \geq 2\sigma(I)$). The molecule appears to be tetranuclear with C_i symmetry. Four tetracoordinated copper atoms are arranged at the corners of a parallelogram, with side lengths of 3.3174 (8) and 3.4159 (8) Å and angles of 81.38 (2) and 98.62 (2)°. All sides are bridged by 3(5)-methylpyrazolate ligands. The short sides are additionally bridged by oxygen atoms of the 1-(1-ethanoyl)-5-methylpyrazolate ligand. The N^2 atom of this ligand completes the coordination sphere of one Cu atom, while the coordination around the other Cu atom is completed by a nitrate group. Magnetic susceptibility measurements (80–310 K) show a strong antiferromagnetic interaction. Supposing that the oxygen bridge is the main pathway for superexchange interaction, the results were fitted to the Bleaney–Bowers equation for dimers, yielding a J value of −202 (1) cm^{-1}.

Introduction

Copper coordination compounds are well-known to act as catalysts in the oxidation of organic molecules such as vitamin C and phenols.[1,2] It has been shown that the catalytic-active species are frequently dimeric copper compounds. Propositions have been made that this dimeric nature may be retained during the catalytic cycle.[2] As the hydroxo and halogen bridges, normally present in these dimers, are rather weak, organic ligands such as oxalate and pyrazolate have been used to obtain stronger bridges. Especially with the pyrazolate ligand, many dimeric and oligomeric coordination compounds have been prepared.[3]

With copper(II) as the metal ion, the number of well-characterized compounds having a pyrazolate bridge is very small and no crystal structure determinations have been reported.[4] The copper(II) compounds are usually obtained as finely divided powders, which are difficult to investigate. Recent work from this laboratory[5] has shown that a procedure starting from copper(I) compounds may yield interesting oxidation products that cannot be obtained otherwise.

The present study was undertaken to see whether or not copper(I) compounds of 3(5)-methylpyrazole could be used as starting materials for pyrazolate-bridged copper(II) compounds of magnetic and catalytic interest. This paper describes the first results of this investigation, showing that not only interesting magnetic structures can be obtained but also that surprising oxidation products may be isolated.

Experimental Section

All reagents were commercially available and used without further purification. $Cu(MPZH)_4(NO_3)_2$ (MPZH = 3(5)-methylpyrazole) was prepared following literature methods.[6]

Synthesis. $Cu^I(MPZH)_2(NO_3)$. A mixture of $Cu(MPZH)_4(NO_3)_2$ (1.93 mmol) and copper powder (3.86 mmol) in diethyl ether (200 mL) was stirred for 5 days in a nitrogen atmosphere. The white precipitate of $Cu^I(MPZH)_2(NO_3)$ was isolated under nitrogen. Anal. Calcd for $C_8H_{12}N_5O_3Cu$: Cu, 21.93. Found: Cu, 21.78.

$Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2$ (MPZ = 3(5)-Methylpyrazolato; AcMPZ = 1-(1-Ethanoyl)-5-methylpyrazolato). Air saturated with water and ethanol was passed over solid $Cu^I(MPZH)_2(NO_3)$ for 1 day. The resulting green solid was dissolved in 1,4-dioxane. After filtration the solvent was removed by evaporation. Then the residue was dissolved in ethanol (100%), and diethyl ether (200 mL) was added. After removal of a white precipitate, an additional amount of diethyl ether (400 mL) was added. Dark blue crystals were formed in a few days. Anal. Calcd for $C_{28}H_{36}N_{14}O_8Cu_4$: Cu, 26.67; C, 35.29; H, 4.03; N, 20.58. Found: Cu, 26.2; C, 35.2; H, 4.03; N, 20.31.

Analysis and Spectral and Magnetic Measurements. The amount of copper was determined by standard EDTA titrations, while C, H, and N analyses were carried out by the Mikroanalytisches Laboratorium of E. Pascher, Bonn, FRG. Infrared spectra (4000–180 cm^{-1}) were recorded on a Model 580 Perkin-Elmer infrared spectrometer using KBr pellets and Nujol mulls. UV–visible spectra (35000–4000 cm^{-1}) were obtained with a Beckman DK-2A ratio recording spectrophotometer by using the diffuse-reflectance technique, with MgO as a reference.

EPR spectra were recorded on Varian E-3 (X-band) and Varian V4500 (Q-band) spectrometers using powdered samples (at room and liquid-N_2 temperatures) and frozen solutions.

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Table I. Final Fractional Coordinates with Esd's in Parentheses[a]

atom	*x/a*	*y/b*	*z/c*	atom[b]	*x/a*	*y/b*	*z/c*
Cu(1)	4109.1 (6)	5681.9 (4)	3147.1 (4)	N(31)	6919 (4)	3814 (4)	3074 (3)
Cu(2)	4572.7 (6)	6360.3 (4)	5672.4 (5)	N(32)	6840 (4)	3259 (3)	3869 (4)
N(11)	3326 (4)	4946 (3)	4005 (3)	C(33)	7919 (7)	2764 (6)	4186 (6)
N(12)	3904 (4)	4122 (3)	4522 (3)	C(34)	8650 (8)	2990 (7)	3603 (7)
C(13)	3131 (5)	3708 (4)	4967 (4)	C(35)	8000 (6)	3669 (6)	2881 (5)
C(14)	2054 (6)	4252 (5)	4736 (5)	C(36)	8328 (8)	4187 (9)	2059 (7)
C(15)	2193 (5)	5008 (4)	4126 (4)	C(37)	5779 (5)	4365 (5)	2494 (4)
C(16)	1255 (6)	5758 (6)	3590 (6)	C(38)	4995 (7)	3761 (7)	1566 (6)
N(21)	4161 (4)	7299 (3)	4533 (3)	O(31)	5121 (3)	4541 (2)	3179 (2)
N(22)	3771 (4)	6997 (3)	3522 (3)	N(41)	3558 (6)	6173 (4)	1145 (4)
C(23)	3387 (6)	7802 (5)	2932 (5)	O(41)	4548 (4)	6221 (3)	1947 (3)
C(24)	3519 (6)	8598 (5)	3539 (5)	O(42)	3612 (6)	6501 (5)	323 (4)
C(25)	4012 (5)	8279 (4)	4545 (5)	O(43)	2611 (5)	5828 (4)	1251 (4)
C(26)	4393 (9)	8822 (6)	5541 (8)				
H(131)	317 (3)	302 (3)	547 (3)	H(261)	519 (5)	891 (5)	574 (5)
H(141)	139 (5)	416 (4)	494 (4)	H(262)	405 (5)	939 (4)	546 (5)
H(231)	309 (5)	767 (4)	229 (4)	H(263)	393 (5)	867 (4)	599 (4)
H(241)	338 (5)	924 (4)	337 (4)	H(361)	777 (5)	406 (4)	145 (4)
H(331)	806 (6)	236 (4)	470 (4)	H(362)	815 (5)	494 (4)	212 (5)
H(371)	608 (4)	495 (4)	229 (4)	H(363)	915 (5)	418 (4)	211 (4)
H(341)	928 (7)	276 (5)	361 (6)	H(381)	425 (5)	411 (4)	120 (4)
H(161)	161 (5)	636 (4)	384 (4)	H(382)	477 (5)	306 (4)	186 (4)
H(162)	79 (5)	552 (4)	282 (4)	H(383)	554 (5)	354 (4)	108 (4)
H(163)	54 (5)	580 (4)	399 (4)				

[a] The fractional atomic coordinates for nonhydrogen atoms are multiplied by 10^4, those for hydrogen atoms are multiplied by 10^3.
[b] The first two figures of the hydrogen atom number point to the number of the attached carbon atom.

X-ray powder diagrams were obtained with a Guinier-de Wolff camera using Cu Kα radiation. Samples were mounted on adhesive tape. This technique was used to establish that samples, obtained in successive preparations, were identical. Magnetic susceptibility measurements (80–310 K) were carried out with use of the Faraday method.

Data Collection. A crystal of approximate size 0.4 × 0.3 × 0.2 mm was mounted in a capillary tube. Weissenberg photographs established the suitability of the selected crystal for single-crystal X-ray analysis. The space group, the unit cell dimensions, and reflection data were obtained from an Enraf-Nonius CAD-4 single-crystal diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The compound crystallizes in the space group $P2_1/n$.[7] The unit cell parameters are a = 11.245 (3) Å, b = 13.690 (4) Å, c = 13.553 (5) Å, $\alpha = \gamma = 90°$, β = 109.31 (3)°, V = 1969 Å^3, d(obsd) = 1.60 g/cm^3 (by flotation), and d(calcd) = 1.61 g/cm^3 for Z = 2.

Reflections were measured by the ω/θ scan technique for $2 < \theta < 24$ with $0 \leq h \leq 13$, $-16 \leq k \leq 16$, and $-16 \leq l \leq 16$. The scanning rate was adjusted to the required precision of $I \geq 2\sigma(I)$, with a maximum scan time of 90 s/reflection. Each reflection was measured in 96 steps; 16 steps at each end of the scan were considered as background. Intensities I and their estimated standard deviations $\sigma(I)$, were calculated from

$$I = s[P - 2(B_1 + B_2)] \qquad \sigma(I) = s[P + 4(B_1 + B_2)]^{1/2}$$

where s is a factor to account for the variable scan speed, P is the scan count, and B_1 and B_2 are the low- and high-angle background counts. The instrument and crystal stability were checked every 5400 s of radiation time by measuring three reference reflections; no significant changes in the intensities were observed.

A total of 6381 reflections was measured, of which 3080 were independent; from these 2124 were considered as observed ($I \geq 2\sigma(I)$). Intensities were corrected for Lorentz and polarization effects. As soon as the molecular structure was known, absorption correction was applied with a Monte Carlo method as described by de Graaff.[8] Before correction, measurements at different azimuthal positions of two reflections showed a variation of 13% in the intensities. The linear absorption coefficient was μ(Mo Kα) = 2.25 mm^{-1}.

Solution and Refinement. The calculations were performed on the Leiden University Amdahl V7B and IBM 370/158 computers, using a local set of computer programs. Scattering factors for neutral atoms have been taken from ref 9, excpet for hydrogen for which the values published by Stewart et al.[10] were used. For all atoms corrections were made for the real part of the anomalous dispersion ($\Delta f'$), while for copper also the imaginary part ($\Delta f''$) was included. The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations. The thermal parameters of all but the hydrogen atoms were anisotropically refined. The function minimized was $\sum(|F_o| - |F_c|)^2$, i.e., unit weights were used. Hydrogen atoms were located from difference-Fourier maps. In the refinement, the protons of the methyl groups were given a fixed value of 6.0 Å^2 for the thermal parameter. At the final stage the conventional discrepancy index R_F $[\sum(||F_c| - |F_o||)/\sum|F_o|]$ had been reduced to 3.1% and the weighted R factor R_{wF} $[[\sum(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}]$ to 3.2% (w = 1). Observed and calculated structure factors are available.[11] Positional parameters are listed in Table I. The most important bond distances are given in Table II. A list of thermal parameters is given in the supplementary material, together with other bond lengths and distances.[11]

Table II. Most Relevant Bond Distances (Å) in $Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2$[a,b]

Cu(1)–Cu(2)	3.4159 (8)	Cu(2)–N(21)	1.944 (4)
Cu(1)–Cu(2)*	3.3174 (8)	Cu(2)*–N(12)	1.933 (4)
Cu(1)–Cu(1)*	5.106 (1)	Cu(2)*–N(32)	1.959 (5)
Cu(2)–Cu(2)*	4.391 (1)	Cu(2)*–O(31)	1.926 (3)
Cu(1)–N(11)	1.954 (4)	Cu(1)–O(43)	2.572 (5)
Cu(1)–N(22)	1.942 (4)	N(41)–O(41)	1.275 (6)
Cu(1)–O(31)	1.924 (3)	N(41)–O(42)	1.220 (6)
Cu(1)–O(41)	1.991 (4)	N(41)–O(43)	1.216 (6)

[a] Atoms assigned with an asterisk are in the equivalent position $1 - x$, $1 - y$, $1 - z$. [b] For the numbering system, see Figure 1.

Results and Discussion

Structure Description. A picture of the title compound with its numbering scheme is provided in Figure 1; hydrogen atoms, except those of the ethanolato part of the AcMPZ ligand, have been omitted for clarity. Figure 2 gives a stereoscopic picture, illustrating the packing of the compound. The most important

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(7) This untabulated space group was used instead of $P2_1/c$ in order to reduce the computer calculation time.

(8) R. A. G. de Graaff, *Acta Crystallogr., Sect. A*, **A29**, 298 (1973).

(9) "International Tables for X-ray Crystallography", Vol. 4, Kynoch Press, Birmingham, England, 1968.

(10) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(11) Supplementary material.

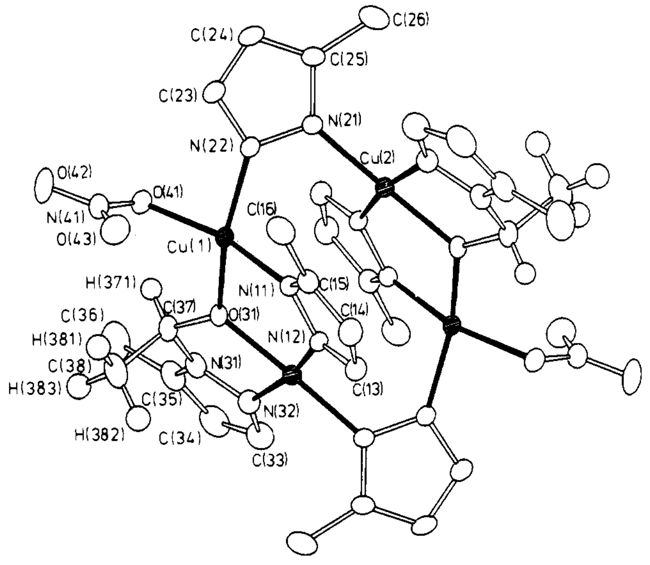


Figure 1. ORTEP projection (probability 15%) of the molecular structure of $Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2$ with the numbering scheme of the symmetry-independent part of the molecule. Unlabeled atoms are in the equivalent position $1 - x$, $1 - y$, $1 - z$ and are referred to in the text by an asterisk in addition to the atom symbol.

Table III. Most Relevant Bond Angles (Deg) in $Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2$[a]

Cu(2)-Cu(1)-Cu(2)*	81.38 (2)
N(11)-Cu(1)-N(22)	99.0 (2)
N(11)-Cu(1)-O(31)	87.0 (2)
N(11)-Cu(1)-O(41)	163.6 (2)
N(22)-Cu(1)-O(31)	155.8 (2)
N(22)-Cu(1)-O(41)	89.6 (2)
O(31)-Cu(1)-O(41)	90.9 (1)
O(41)-Cu(1)-O(43)	54.0 (2)
Cu(1)-Cu(2)-Cu(1)*	98.62 (2)
N(12)-Cu(2)*-N(21)*	96.1 (2)
N(12)-Cu(2)*-N(32)	169.2 (2)
N(12)-Cu(2)*-O(31)	87.8 (1)
N(21)*-Cu(2)*-N(32)	94.1 (2)
N(21)*-Cu(2)*-O(31)	176.1 (2)
N(32)-Cu(2)-O(31)	82.0 (2)
Cu(1)-O(31)-C(37)	124.6 (3)
Cu(1)-O(31)-Cu(2)*	119.0 (2)
Cu(2)*-O(31)-C(37)	115.9 (3)
Cu(1)-O(41)-N(41)	107.2 (4)
Cu(1)-O(43)-N(41)	80.7 (3)
O(41)-N(41)-O(42)	117.8 (6)
O(41)-N(41)-O(43)	118.1 (5)
O(42)-N(41)-O(43)	124.1 (7)
N(31)-C(37)-O(31)	107.1 (4)
N(31)-C(37)-C(38)	109.1 (6)
O(31)-C(37)-C(38)	110.9 (5)

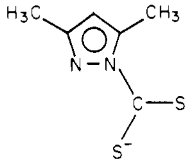
[a] Atoms assigned with an asterisk are in the equivalent position $1 - x$, $1 - y$, $1 - z$.

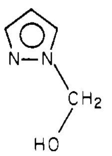
bond distances and angles are given in Tables II and III, respectively. Other geometrical information is available as supplementary material.[11] The molecules of the title compound (two per unit cell) are tetranuclear with C_i symmetry. Their structure is built up by four copper atoms, arranged at the corners of a parallelogram, with side lengths of 3.3174 (8) (Cu(1) – Cu(2)*) and 3.4159 (8) Å (Cu(1)–Cu(2)). The angles are 81.38 (2)° (Cu(2)–Cu(1)–Cu(2)*) and 98.62 (2)° (Cu(1)–Cu(2)–Cu(1)*). All four sides are bridged by MPZ ligands. The short sides of the parallelogram are additionally bridged by the oxygen atoms of the AcMPZ ligands. The two AcMPZ ligands are furthermore bonded to two copper atoms Cu(2) and Cu(2)* via the pyrazolyl N^2 atoms (Cu(2)–N(32) and Cu(2)*–N(32)*). Nitrate ions are bonded to the other copper atoms via one oxygen atom (Cu(1)–O(41) and Cu(1)*–O(41)*). A second nitrate oxygen atom is at a semicoordinating distance of Cu(1) and Cu(1)*. The discrete molecules are well separated with normal van der Waals interatom distances.

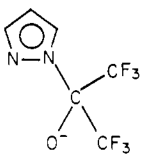
The above described coordination accounts for the presence of two types of copper atoms. The coordination sphere of the first type (Cu(1)/Cu(1)*) is formed by two nitrogen (N(11) and N(22)) and two oxygen atoms (O(31) and O(41)). The geometry is tetrahedrally distorted square planar, with trans-atom bond angles much smaller than 180°: O(31)–Cu(1)–N(22) = 155.8° and O(41)–Cu(1)–N(11) = 163.6°. The tetrahedral distortion is furthermore reflected by the distances of the five atoms concerned to the least-squares plane through these atoms: Cu(1), 0.06; O(31), –0.4; O(41), 0.3; N(11) 0.3; N(22), –0.3 Å.

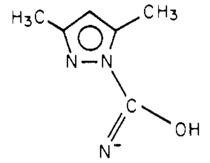
The second type of copper atoms (Cu(2)*/Cu(2)) is coordinated by three nitrogen atoms (N(12), N(21)*, and N(32)) and one oxygen atom (O(31)) and has an almost planar geometry, with distances of the atoms to the least-squares plane not exceeding 0.04 Å. However, a small in-plane distortion is observed, as is visualized by the bond angles O(31)–Cu(2)*–N(21)* = 176.1° and N(12)–Cu(2)*–N(32) = 169.2°. The pyrazole rings are normal, deviation from least-squares planes not exceeding 0.04 Å.

A surprising aspect of the crystal structure is the presence and the structure of the AcMPZ ligands, apparently formed by reaction of acetaldehyde (formed from ethanol and oxygen in the presence of copper) with pyrazole or pyrazolate ligands. Such additions of electrophiles to the pyrazole nitrogen have been observed before for molecules such as CS_2,[12] formaldehyde,[13] $(CF_3)_2CO$,[14] and even the cyanate anion,[15] resulting in ligands such as

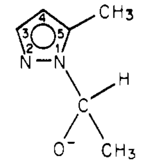








Only in case of cyanate, however, such an addition has been observed in the presence of copper ions.[15] It should be noticed that, contrary to the addition products with CS_2 and NCO^-, the carbon atoms at the 1-position of the pyrazole group in our ligand are tetrahedrally coordinated, suggesting single N–C and C–O bonds. The bridging oxygen atom bears no proton, as is further seen from the copolanarity of the unit O(31)–Cu(1)–Cu(2)*–C(37).



The methyl group in the AcMPZ ligand, i.e., C(36), is located

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(15) F. Valach, J. Kohout, M. Dunaj-Jurco, M. Hvastijova, and J. Gazo, *J. Chem. Soc., Dalton Trans.*, 1867 (1979).

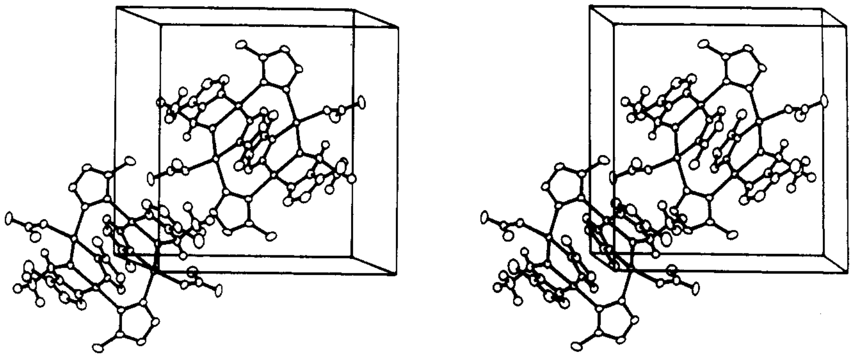

Figure 2. Stereoscopic view showing the unit cell content and the molecular packing.

in position 5 of the pyrazole ring, just as observed before in some other coordination compounds prepared from 3(5)-methylpyrazole.[16] The location of the methyl group at position 5 suggests that the attack by acetaldehyde has taken place after coordination of N(2) to Cu. Otherwise the methyl group should also be present in position 3. The nitrate ligand is entirely planar (deviations from the least-squares plane being less than 0.01 Å). The coordination to copper occurs predominantly via one oxygen atom (Cu(1)–O(41) = 1.99 Å). The differences in N-O bond lengths are in agreement with this description: N(41)–O(41) = 1.275, N(41)–O(42) = 1.22, and N(41)–O(43) = 1.22 Å. Nevertheless, the distance of O(43) to Cu(1) is relatively short: 2.57 Å. Such an interaction has been observed in related compounds.[17] The position of Cu(1) in the plane of the nitrate ligand (according to least-squares calculations) supports such a weak bonding, although the Cu(1)–O(43)–N(41) angle (80°) is rather small.

Spectroscopy and Magnetism. As can be seen from the X-ray structure, the tetranuclear molecule contains two kinds of $\mathrm{Cu^{II}}$ ions. Cu(2) is almost square-planar coordinated, whereas Cu(1) has a significant distortion toward tetrahedral geometry. Also the donor sets for both metals are different: Cu(1) has an N_2O_2 environment whereas Cu(2) has an N_3O environment. Given this situation one might expect two different absorption maxima in the ligand field spectra. However, only one broad band at 16 300 $\mathrm{cm^{-1}}$ is observed, indicating that the differences in the orbital levels for both copper ions are too small to yield separated ligand field transitions.

As is already clear from the molecular structure, the copper ions can be expected to be magnetically coupled. Therefore the temperature dependence of the magnetic susceptibility was studied. The results of the measurements on a powdered sample, with a Faraday balance, are depicted in Figure 3. The molar susceptibilities have been corrected for diamagnetism, using Pascal constants as given in ref 18. As the figure shows, the maximum χ value will be reached well above room temperature. At 300 K the magnetic moment μ_{eff} amounts to only 1.26 μ_{B}/copper atom. The observed susceptibilities were fitted to a theoretical model. Since it is generally accepted that the interaction between unpaired spins occurs via σ pathways through the bridging ligands, the present situation can be described by the Hamiltonian

$$\mathcal{H} = -2(J_{\mathrm{a}}S_1S_2 + J_{\mathrm{b}}S_1{\cdot}S_2)$$

in which the numeral indices point to the copper atom symbols. As these two J values cannot be determined separately by a fitting procedure,[19] the above Hamiltonian has been reduced to

$$\mathcal{H} = -2JS_1S_2$$

describing the situation as met in copper dimers and assuming that J_{a} differs strongly from J_{b}. The observed data were therefore fitted to the Bleaney–Bowers equation[20]

$$\chi_{\mathrm{M}} = (1-\rho)\frac{N\beta^2g^2}{kT}(3 + e^{-2J/kT})^{-1} + \frac{0.405\rho}{T} + N\alpha$$

in which ρ accounts for the fraction of monomeric impurities and N for the temperature-independent paramagnetism (TIP). With $N\alpha = 60.0 \times 10^{-6}$ $\mathrm{cm^3\ mol^{-1}}$/copper atom, a least-squares procedure led to $g = 2.245$, $J = -202.1$ $\mathrm{cm^{-1}}$, and $\rho = 0.8\%$. The calculated curve based on these data is also represented in Figure 3. The good quality of the fit to the dimer equation suggests that the assumption that J_{a} differs strongly from J_{b} is valid. The question then remains which of the possible pathways (Cu(1)–Cu(2)*, via the oxygen and pyrazolate bridge, or Cu(1)–Cu(2), via the pyrazolate bridge only) is the important one. Recent publications have shown that pyrazolate bridges generally result in weaker antiferro-

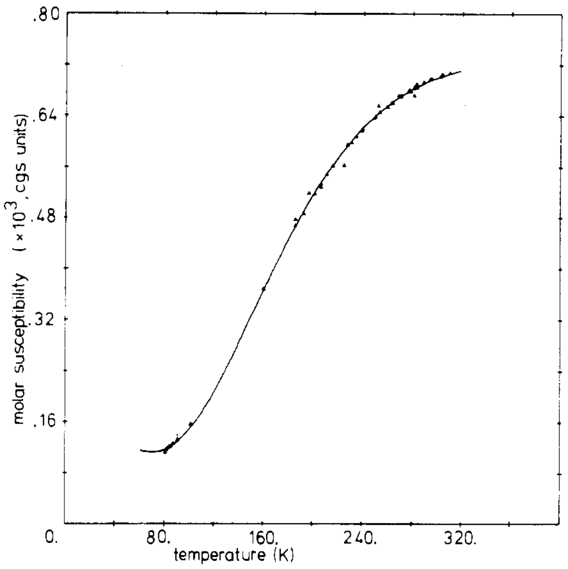

Figure 3. Temperature dependence of the magnetic susceptibility of $\mathrm{Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2}$: (▲) observed χ_{mol} values ($\mathrm{cm^3\ mol^{-1}}$/Cu atom) corrected for diagmagnetism; (—) theoretical curve according to the Bleaney–Bowers equation for dimers, with $J = -202$ (1) $\mathrm{cm^{-1}}$, $g = 2.24$, and TIP = 60.0×10^{-6} $\mathrm{cm^{-3}/mol^{-1}}$, including 0.8% of a monomeric impurity.

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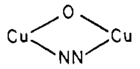
magnetic interactions (up to $-100\ cm^{-1}$)[21] than substituted-oxide bridges.[22-24] With the assumption that the exchange via the oxygen atom is the most important, the actual J value is relatively small in view of what can be expected from a correlation between the J value and the Cu–O–Cu angle, as reported by Hatfield et al.[25] Although the observed bridge angle (Cu(1)–O(31)–Cu(2)* = 119.0°) is far beyond the region in which the linear relationship has been observed, a $2J$ value of $-1600\ cm^{-1}$ would be expected.[25] Even compared with the pyridine N-oxide bridged systems[23] ($2J \approx -900$), the observed J value is very small. The distortion of the geometry of the Cu(1) atom from square planar toward tetrahedral, as additionally seen from the angles between the O(31)–Cu(1)–O(41) and N(11)–Cu(1)–N(22) planes (that amounts to 27.7°), may be the main reason for the small J value. In this case the magnetic orbital for Cu(1) may not be entirely $d_{x^2-y^2}$, bringing the direction of the molecular orbital containing the unpaired spin density out of the Cu_4 plane[22,26-29] and reducing the exchange interaction.

So that further information about the electronic structure of the tetranuclear compound could be obtained, EPR spectra were recorded. When the approximation of magnetic dimers would be valid, one might expect triplet EPR spectra.[30] However, spectra recorded both at X-band and at Q-band frequencies (77 and 300 K) did only show broad, structureless bands, indicating that either the coupling between the dimers is too strong to observe triplet spectra or the zero-field splittings in the triplet states are too large (larger than the Q-band frequency) to be observed.

Concluding Remarks

The present study has made clear that interesting, new coordination compounds of Cu^{II} may be obtained by oxidation of Cu^{I} coordination compounds. One should however be aware of the occurrence of side reactions, as met in the present preparation. As is shown, the solvent was oxidized and a reaction of the oxidized product with the ligand 3(5)-methylpyrazole followed, giving an interesting new type of ligand. Although the mechanism of formation is not clear, it is evident that both the moist air and the ethanol play a key role in the formation of the title compound. The observed, relatively weak magnetic exchange within the tetranuclear cluster might be due to the fact that half of the copper ions has a magnetic orbital which is not coplanar with the unit



Further studies in which different pyrazole ligands and counterions are used are in progress.

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Registry No. $Cu_4(MPZ)_4(AcMPZ)_2(NO_3)_2$, 80997-18-8; $Cu^I(MPZH)_2(NO_3)$, 81011-46-3; ethanol, 64-17-5; $Cu(MPZH)_4(NO_3)_2$, 41667-46-3.

Supplementary Material Available: A listing of structure factor amplitudes, tables of thermal parameters of all atoms, and additional information about bond angles and bond distances for the ring systems and hydrogen to carbon and nitrogen bonds (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Reactivity of Bis(1,4-diaryltetraazabutadiene)nickel Complexes. Crystal and Molecular Structure of Bis[1,4-bis(3,5-dimethylphenyl)tetraazabutadiene]nickel

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Bis(tetraazabutadiene)nickel complexes, $[Ni(Ar_2N_4)_2]$, have been prepared by reactions of bis(1,5-cyclooctadiene)nickel or bis(cyclopentadienyl)nickel with aryl azides (Ar = $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}ClC_6H_4$, and $3,5\text{-}Me_2C_6H_3$). The reaction with bis(cyclopentadienyl)nickel proceeds via $[Ni(Ar_2N_4)(\eta^5\text{-}C_5H_5)]$. The crystal and molecular structure of bis[1,4-bis(3,5-dimethylphenyl)tetraazabutadiene]nickel, which is the first example of a bis(tetraazabutadiene)metal complex, have been determined by a single-crystal X-ray diffraction study. Crystals are tetragonal, space group $P4_2/n$, with $Z = 2$ in a unit cell of dimensions $a = b = 9.677$ (1) and $c = 16.601$ (1) Å. The final R value is 0.034 for 1307 reflections. The nickel atom has a pseudotetrahedral geometry with two planar Ar_2N_4 ligands orientated perpendicular to each other. Furthermore the three N–N bond distances are nearly equal with a mean value of 1.322 Å. On the basis of these structural features the compounds are formulated as 18e Ni^0 species. Bis[1,4-bis(4-tolyl)tetraazabutadiene]nickel reacts with *tert*-butyl isocyanide to give $[Ni[1,4\text{-}(4\text{-}MeC_6H_4)_2N_4](t\text{-}BuNC)_2]$. The latter product could also be prepared via the 1/1 reaction of $[Ni[1,4\text{-}(4\text{-}MeC_6H_4)_2N_4]_2]$ with $[Ni(t\text{-}BuNC)_4]$ in the presence of excess t-BuNC.

Introduction

The reactions of organic azides with transition-metal complexes have attracted considerable attention in recent years. Among the products are isocyanate (RNCO), imido (RN), ureylene (RNCONR), imino (RHN), and tetraazabutadiene (RN_4R) derivatives.[1]

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