Spectroscopic and Magnetic Identification of Difluoro-bridged Zigzag Copper Chains with Substituted 5-Phenylpyrazole Ligands. Structural Identification of *catena*-Poly[bis(3-methyl-4-ethyl-5-phenylpyrazole)copper-di-μ-fluoro]

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(Received February 28, 1989)

Abstract

The synthesis, spectroscopic and magnetic properties of compounds from $CuF_2 \cdot 2H_2O$ and substituted 5-phenylpyrazoles are reported. The ligands used are 5-phenylpyrazole (abbreviated ppzH), 3,4-dimethyl-5-phenylpyrazole (dmppzH) and 3-methyl-4-ethyl-5-phenylpyrazole (meppzH). The crystal structure of $[CuF_2(meppzH)_2]_\infty$ has been determined. The compound crystallized in the space group $P\bar{1}$; triclinic; $a = 13.888(6)$, $b = 5.671(3)$, $c = 15.181(6)$ Å, $\alpha = 91.95(4)°$, $\beta = 111.56(3)°$, $\gamma = 92.39(4)°$, $Z = 2$, $R(R_w) = 0.0420(0.0581)$, with Cu–Cu′ = 3.3295(7) and Cu–Cu″ = 3.2935(7) Å. The monomeric unit consists of a chromophore CuN_2F_2 in a tetrahedrally distorted square plane with *cis* coordinated substituted N-donor pyrazoles at a distance of 1.992(2) and 1.996(2) Å and *cis* coordinated fluoride anions at a distance of 1.916(2) and 1.915(2) Å. Axial ligands are two fluoride anions of the nearby copper atoms of the next units along the chain, coordinated at distances of 2.448(2) and 2.400(2) Å, respectively. The so-formed zigzag chain consists of two different CuF_2Cu units positioned along the *b* axis.

The structure is related to the spectroscopic and magnetic properties of the compounds. The infrared spectra show a strongly shifted N–H stretching vibration around 2800 cm^{-1} and Cu–F vibrations near 400 and 450 cm^{-1}. The EPR spectra at room temperature show an isotropic signal at $g = 2.13$ for dmppzH and meppzH and an anisotropic signal with $g_\perp = 2.09$ and $g_\parallel = 2.31$ for ppzH. No hyperfine splitting is observed. At 77 K a weak half-field signal appears with $g = 4.11$.

Magnetic measurements in the region 4–300 K indicate a predominant paramagnetic character for all compounds. However, at very low temperatures (anti)ferromagnetism becomes apparent. The data, fitted on an isotropic linear chain with $S = \frac{1}{2}$ and $H = -2J\Sigma S_i \cdot S_j$, gave the best-fit parameters $J = 0.3$ cm^{-1} and $g = 2.23$ for $CuF_2(meppzH)_2$, $J = 1.4$ cm^{-1} and $g = 2.22$ for $CuF_2(ppzH)_2$ and $J = -0.1$ cm^{-1} and $g = 2.16$ for $CuF_2(dmppzH)_2$.

Introduction**

The formation of fluoride containing compounds is possible with controlled fluoride release through BF_4^- decomposition in the presence of azole ligands [2, 3]. The compounds formed by this method often contain both BF_4^- and F^- anions. A variety of such compounds is known in the literature [4, 5]. Examples of the different types of compound are dimeric and cluster compounds of the formula $[M_nF_nL_x]^{n+}(BF_4)_n$ (L = azole ligand; M = Cu, Co: $n = 1, x = 2n$ or $3n$; M = Cu, Co, Cd, Mn, Ni: $n = 4, x = 3n$). However, the linear-chain compounds formed by this method contain no BF_4^- [6]. The number of X-ray structures for this type of compound is rather small, apparently due to the difficulty in growing single crystals. Quite often only metal fluorides without ligands are obtained. For ppzH, this method resulted in a SiF_6-bridged copper chain [7].

Another method of synthesizing fluoride containing coordination compounds is the use of metal fluorides. These salts are insoluble, or at best poorly soluble, in organic solvents [8], but in the presence of some ligands or in a suitable solvent the solubility of these salts can be improved [9]. This method has resulted in a limited number of coordination compounds [10–12].

Using hydrated copper(II) fluoride and substituted 5-phenylpyrazole (see Fig. 1) in methanol, crystalline

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**For nomenclature see ref. 1.

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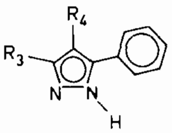

Ligand	R1	R2
ppzh	H	H
dmppzH	CH$_3$	CH$_3$
meppzH	CH$_3$	C$_2$H$_5$

Fig. 1. 5-Phenylpyrazole derivates.

products have been isolated with the formula CuF$_2$L$_2$, which will be described in this study. The spectroscopic and magnetic analyses indicate that these compounds probably have a mutually similar structure. Infrared spectra show the presence of Cu–F vibrations and a N–H stretching vibration, strongly shifted to lower frequency, in all compounds. Ligand field spectra of the compounds indicate almost identical environments for the copper(II) ions.

EPR measurements indicate polynuclear compounds. Magnetic measurements down to 4 K revealed a paramagnetic behaviour. The structure of one of the compounds, [CuF$_2$(meppzH)$_2$]$_\infty$, was solved to study this behaviour with detailed structural information. A preliminary report on this X-ray structure has already appeared [13].

Experimental

Commercially available CuF$_2$·2H$_2$O was used without any further purification.

The ligands ppzH, dmppzH and meppzH were prepared from their substituted β-diketones and hydrazine [6, 14–16], using known methods.

Preparation of the Coordination Compounds

Compounds of the formula CuF$_2$L$_2$ (L = ppzH, dmppzH, meppzH) were synthesized by adding a warm solution of 4 mmol of L in 25 ml methanol to a suspension of 1 mmol CuF$_2$·2H$_2$O in 25 ml warm methanol. After a few minutes of heating the non-dissolved copper fluoride was filtered off. The resulting green solution was kept in a polyethene vessel until a blue crystalline product precipitated. Single crystals of the compound CuF$_2$meppzH$_2$ were synthesized similarly: the mixture of meppzH and copper fluoride was stirred for several minutes. After removing the non-dissolved salt, the clear green solution was kept in a polyethene vessel for three weeks to give blue needles. See ‘Supplementary Material’.

Spectroscopic and Magnetic Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 580 B IR spectrophotometer in the region of 4000–250 cm^{-1}. Samples were measured as KBr pellets. Ligand field spectra in the region of 33000–5000 cm^{-1} were taken on a Perkin-Elmer 330 UV–Vis spectrophotometer using the diffuse-reflectance technique with MgO as a reference. EPR spectra were recorded on a Varian E3 (9.5 GHz) spectrometer using powdered samples. Magnetic measurements from powdered samples were performed on a Faraday balance in the temperature region 4–300 K as described earlier [17, 18]. Elemental analyses were executed by Micro-analytical Laboratory, University College, Dublin, Ireland.

X-ray Analyses

A single crystal was selected and mounted on an Enraf-Nonius CAD-4 automatic diffractometer, following the ω–2θ scanning method. Mo Kα radiation (λ = 0.71073 Å), monochromated by graphite, was used to determine the unit-cell parameters, the space group as well as the reflection intensities at room temperature. The collected data were corrected for Lorentz and polarization effects and for absorption [19]. Diffraction and crystal data are summarized in Table 1. The observed density was determined by flotation in a mixture of 1,3-dibromopropane and n-hexane. All calculations were performed on the Leiden University (IBM) Computer. The position of Cu was determined by means of a Patterson synthesis. The neighbour atoms of the metal were found using MULTAN. The non-hydrogen atoms were found from the observed difference Fourier maps and refined by least-squares methods. The function minimized during least squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with $w = \sigma_F^{-2}$. For one ethyl carbon (C38) (see Fig. 2), three different positions were found, caused by disorder in the structure. The disorder around

TABLE 1. Crystal and diffraction data for [CuF$_2$(meppzH)$_2$]$_\infty$

Molecular formula	C$_{24}$H$_{28}$CuF$_2$N$_4$
Molecular weight	474.03
Space group	$P\bar{1}$
Lattice constants	
a (A)	13.888(6)
b (A)	5.671(3)
c (A)	15.181(6)
α (°)	91.95(4)
β (°)	111.56(3)
γ (°)	92.39(4)
Z	2
θ range (°)	2–36
Range of indices	
h	−23 to 23
k	−9 to 9
l	0 to 25
F(000)	471
No. independent reflections	10884
No. significant reflections	5432
Final R	0.0420
Final R_w	0.0581
D_{obs} (Mg m^{-3})	1.42
D_{calc} (Mg m^{-3})	1.42
μ (cm^{-1})	10.197

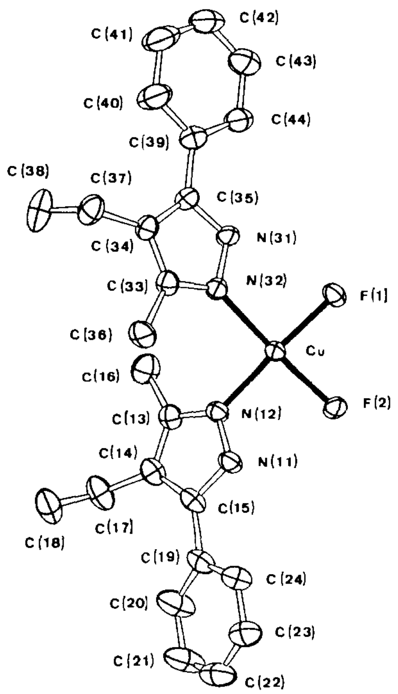

Fig. 2. ORTEP drawing and atomic labelling system for the monomeric unit of $[CuF_2meppzH_2]_\infty$.

carbon C38 was solved using Waser constraints [20]. The carbon–carbon distance between C34 and C37 was fixed at 1.54 Å, the angle between carbon C34–C37–C38 was set to be 110°. The non-hydrogen atoms, except C38, were refined anisotropically. Carbon C38 was refined isotropically. Hydrogen atom positions were calculated and the hydrogen atoms were kept at a fixed distance (0.975 Å) from the parent atom. The hydrogen atoms of the methyl group and of the ethyl CH_3 could not be located, due to the thermal motion. The hydrogen atoms found were refined isotropically with one B value. Further refinement of $R = \Sigma(|F_o| - |F_c|/|F_o|)$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ led to convergence with $R = 0.0420$ and $R_w = 0.0581$. See also 'Supplementary Material'.

Results and Discussion

Description of the Structure

Relevant bond lengths and bond angles are listed in Table 2. A projection of the unit $CuF_2(meppzH)_2$ with the atomic labelling is shown as an ORTEP [21] drawing in Fig. 2. Coordinated to the copper(II) ion are two nitrogen pyrazole atoms and two fluoride ions in a tetrahedrally distorted square planar *cis* configuration. The distances of Cu–N are 1.992(2) and 1.996(2) Å, respectively. The bond lengths of Cu–F are 1.916(2) and 1.915(2) Å.

TABLE 2. Selected bond distances and angles in $[CuF_2(meppzH)_2]_\infty$

Bond distances (Å)		Bond angles (°)	
Cu–Cu′	3.3295(7)	F(1)–Cu–F(2)	88.66(8)
Cu–Cu″	3.2935(7)	N(12)–Cu–N(32)	95.9(1)
Cu–F(1)′	2.448(2)	Cu–F(1)–Cu′	98.70(6)
Cu–F(2)″	2.400(2)	Cu–F(2)–Cu″	98.89(6)
Cu–N(12)	1.992(2)	F(1)–Cu–F(1)′	82.30(6)
Cu–N(32)	1.996(2)	F(2)–Cu–F(2)″	81.11(6)
Cu–F(1)	1.916(2)	Cu′–Cu–Cu″	117.79(2)
Cu–F(2)	1.915(2)	N(11)–H(11)–F(1)″	145.76(9)
C(16)–C(36)	3.629(5)	N(31)–H(31)–F(2)′	142.32(9)
F(1)–N(11)″	2.693(3)		
N(31)–F(2)′	2.714(3)		
H(11)–F(1)″	1.830(3)		
H(31)–F(2)′	1.876(3)		

Primed atoms are generated by summetry operations: ′ = 1.00 − x, 0.00 − y, 1.00 − z; ″ = 1.00 − x, −1.00 − y, 1.00 − z.

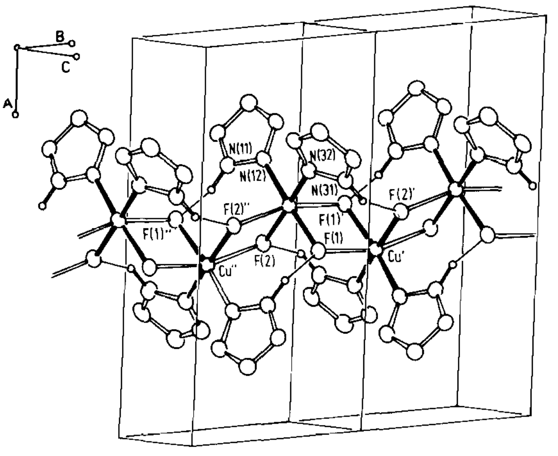

Fig. 3. ORTEP drawing and atomic labelling system for a part of two unit cells of the compound $[CuF_2meppzH_2]_\infty$. Primed atoms are generated by symmetry operations: ′ = 1 − x, −y, 1 − z; ″ = 1 − x, −1 − y, 1 − z.

Planes have been calculated through the pyrazole ring systems in the unit. The angle between the calculated planes is 69.0(2)°. This is an indication for the hindrance between the methyl carbons (C(16)–C(36)). The carbon–carbon distance is 3.629(5) Å.

Axial ligands of the copper(II) ion are fluoride ions, related to the central CuF_2L_2 unit by centres of inversion symmetry. A projection of a part of two unit cells is depicted in Fig. 3. The bond lengths of the axial fluoride ligands are significantly longer than those in the equatorial position. The Cu–F(1)′ bond length is 2.448(2) Å and the Cu–F(2)″ bond length is 2.400(2) Å. The axial ligands make an angle around the copper of 163.84(5)°. The distances between Cu–Cu′ and Cu–Cu″ are 3.330(2) and 3.294(2) Å, respectively. The Cu′–Cu″ distance is equal to the length of the *b* axis. Thus, the zigzag chain consists of CuF_2Cu units, which are positioned along the *b* axis. Hydrogen bridging between the pyrazole N–H and the fluoride ions of the monomeric unit of the next nearby copper is observed, with the N–F bond lengths of 2.693(3) and 2.714(3) Å. The angles of N–H–F are 145.76(9)° and 142.32(9)°. Intramolecular hydrogen bridging, though weaker, has also been reported for mononuclear pyrazole (pzH) metal halide coordination complexes, such as $Ni(pzH)_4Cl_2$, in which the hydrogen bonding system holds the chloride ions in coordination position [22]. In the present structure, the importance of the hydrogen bonding system can be illustrated with the change of the $CuF_2{\cdot}2H_2O$ conformation to that of the described $CuF_2(meppzH)_2$ chain. $CuF_2{\cdot}2H_2O$ possesses a *trans* chain configuration [23, 24], stabilized by intermolecular hydrogen bridging from the coordinated water molecules [25]. The strong tendency of fluoride ions and pyrazole N–H apparently forces the coordination complex to form the *cis* conformation. The observed *cis* configuration of the monomeric unit enables the stabilizing hydrogen bridging between the units. If these monomeric units possessed a *trans* configuration as found for other halide bridged transition metal chains [26, 27], the hydrogen bridging between the units would become impossible, due to unfavorable bond angles and distances.

Spectroscopic Analyses of CuF_2L_2

MeppzH

The infrared spectrum of $CuF_2(meppzH)_2$ shows the presence of a strong decrease in the ν(N–H) stretching mode to around 2840 cm^{-1}, due to N–H..F hydrogen bridging. When the N..F distance is known, the shift in the ν(N–H) stretching mode from 3450 cm^{-1} in the free ligand can be approximated with the formula $\Delta\nu\,(cm^{-1}) = 50[(d/R)^{12} - (d/R)^6]$ in which d is 3.4 and R is the distance between nitrogen and fluoride [28]. The calculated shift corresponds to the observed shift. For $R = 2.693$ Å (see Table 3), the calculated ν(N–H) absorption is 2832 cm^{-1}; for $R = 2.714$ Å, the ν(N–H) is 2894 cm^{-1}, in nice agreement with the observed 2840 cm^{-1}. In fact the 2890 band is overlapped by the ν(C–H) (alkyl) stretching mode. The γ(N–H) out-of-plane at 515 cm^{-1} is sharper than in the free ligand spectrum. Very strong absorption peaks at 776 and 694 cm^{-1} are caused by γ(C–H) out-of-plane (arom.). The hindrance between the methyl groups also becomes apparent. The absorption at 1020 cm^{-1}, due to δ(C–CH), increases and γ($C–CH_3$) at 1195 cm^{-1} decreases, compared to the free ligand spectrum. Two Cu–F vibrations are observed at 455 and 405 cm^{-1}. This area is close to known vibrations for related compounds [29]. Cu–N vibrations could not be assigned with certainty, because of the large number of ligand vibrations in the far-infrared spectrum.

TABLE 3. Magnetic data for CuF_2L_2 (see text for detailed information)

Compound	Calculated		Experimental μ_{eff}	
	J (cm^{-1})	g	4 K	300 K
$CuF_2(ppzH)_2$	+1.4	2.22	2.28	1.97
$CuF_2(dmppzH)_2$	−0.1	2.16	1.83	1.99
$CuF_2(meppzH)_2$	−0.3	2.23	1.86	2.07

The ligand field spectrum of this compound shows a broad absorption with a maximum at 13 870 cm^{-1} and a shoulder at 12 700 cm^{-1}, which indicates a tetragonally distorted octahedral geometry for copper(II) [30, 31]. The maximum is at lower energy than other compounds with a related pseudo-tetragonal coordination environment [30, 31]. This might be caused by the presence of four weak fluoride ligands in a $CuN_2F_2F_2'$ chromophore, observed in the X-ray analysis.

The EPR spectrum of $CuF_2(meppzH)_2$ at room temperature shows an isotropic signal with a g value of 2.13. It also shows exchange narrowing and no hyperfine splitting is observed. Cooled to 77 K, a half-field signal with a g value of 4.11 becomes visible.

DmppzH and ppzH

The spectroscopic analyses results for both $CuF_2(dmppzH)_2$ and $CuF_2(ppzH)_2$ are similar to those of $CuF_2(meppzH)_2$. The infrared spectrum of $CuF_2(dmppzH)_2$ shows the presence of a strong shift in the ν(N–H) stretching mode at 2820 cm^{-1}, due to hydrogen bridging of N–H...F. With almost the same ν(N–H) shift, the calculated N..F distance is the same as found in $CuF_2(meppzH)_2$. The γ(N–H) out-of-plane at 515 cm^{-1} is again sharper than in the free ligand spectrum. Very strong absorption peaks at 772 and 695 cm^{-1} are due to γ(C–H) out-of-plane (arom.). The hindrance between the methyl substituent of the pyrazole rings becomes apparent as δ($C–CH_3$) at 1015 cm^{-1} increases and γ($C–CH_3$) at 1200 cm^{-1} decreases, compared to the free ligand spectrum. The two Cu–F vibrations are observed at 450 and 401 cm^{-1}. The infrared spectrum of $CuF_2(ppzH)_2$ is less complicated than for the other two pyrazole derivates. The infrared spectrum of this compound only consists of aromatic ring vibrations and vibrations resulting from complexation. This compound shows a very strong shift to lower frequency in the N–H stretching vibration, indicating a very strong hydrogen bonding. The approximated

N..F distance [28] would be 2.64 Å. Cu–F vibrations are ascribed to 445 and 395 cm^{-1}. Ligand field spectra of all three described compounds have the same absorption maximum at 13 870 cm^{-1}, suggesting the other two compounds to have the same geometry around copper as found for $CuF_2(meppzH)_2$. EPR measurements of $CuF_2(dmppzH)_2$ revealed the same behaviour as for $CuF_2(meppzH)_2$. At room temperature, the spectrum shows an isotropic signal with a g value of 2.10. At 77 K, this signal is shifted to 2.14. Furthermore, a weak half-field signal with the g value of 4.38 is observed. For the compound with pppzH as ligand, an anisotropic spectrum, with $g_\perp$ value of 2.09 and $g_\parallel$ value of 2.31, is measured at room temperature. Cooled to 77 K, a weak half-field signal is measured with g value of 4.27. These weak half-field signals, usually found for dimers, are not understood at the moment.

Magnetic Susceptibility Measurements

To study magnetic properties of the compounds, magnetic susceptibility measurements were performed in the temperature region of 4–300 K. The resulting curves were corrected for diamagnetism, using Pascal constants. Down to 4 K, no maximum was observed in the χ versus T curves for all compounds, indicating paramagnetic, or very weakly (anti)ferromagnetic coupled, compounds. The μ_{eff} is different for the three compounds only in the very low temperature area. For the substituted 5-phenylpyrazole ligands a small decrease is observed in the μ_{eff}, indicating a weak antiferromagnetic coupling [32]. The unsubstituted 5-phenylpyrazole shows an increasing μ_{eff}, indicating a weak ferromagnetic coupling. These data were fitted on an isotropic linear-chain compound with $S = \frac{1}{2}$ and $H = -2J\Sigma S_i \cdot S_j$ [26a] (see Fig. 4). The resulting g and J values are listed in Table 3. The magnetic orbital in the observed geometry consists mainly of the $d_{x^2-y^2}$ orbital, which is situated in the CuN_2F_2 plane. For the different monomeric units the $d_{x^2-y^2}$ orbitals are parallel. Therefore, the direct overlap between these orbitals is zero. The exchange via the d_{z^2} orbital to the fluoride of the next unit can be considered to be very small. Thus, the magnetic interaction between the copper(II) ion in the units is very weak.

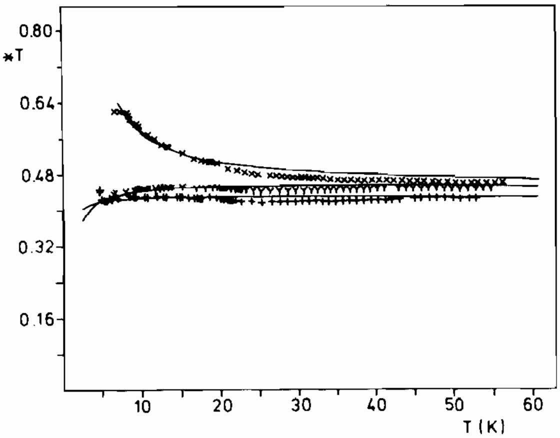

Fig. 4. Magnetic fits of CuF_2L_2 to a model for an isotropic linear chain.

Conclusions

The described 5-phenylpyrazole derivates react with $CuF_2 \cdot 2H_2O$ to form polynuclear coordination compounds, stabilized by strong next-nearest hydrogen bridging, which consists of *cis* coordinated monomeric units. The calculated ν(N–H) shifts to lower frequency for known N–F distances, are in agree with the observed ν(N–H). The resulting coordination compounds have a very weak (anti)-ferromagnetic interaction, which can be understood from the almost parallel and orthogonal $d_{x^2-y^2}$ orbitals.

Supplementary Material

The following tables are available from the authors on request: Table SI, elemental analyses; Tables SII and SIII, positional and anisotropical parameters for the non-hydrogen atoms; Table SIV, the positional and isotropical parameters of the hydrogen atoms; Table SV and SVI, relevant interatomic distances and angles; Table SVII, calculated planes in the compound $CuF_2(meppzH)_2$.

Acknowledgements

We thank Mr S. Gorter for assistance with the X-ray data collection. This research was sponsored by the Netherlands Organization for Chemical Research (SON) with support of the Netherlands Organization for the Advancement of Pure Research (NWO) and the Leiden Materials Science Center (Werkgroep Fundamenteel Materialenonderzoek).

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