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Pyrazoles and Imidazoles as Ligands. XV.* Preparation, Spectra and Magnetic Properties of di-μ-hydroxo-bis-[di(2-methylimidazole)copper(II)] diperchlorate dihydrate

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The preparation of the title compound is reported from $Cu(ClO_4)_2$, 2-methylimidazole and a small amount of water in ethanol solution. The compound consists of dimeric units $[(2MIz)_2Cu(OH)]_2^{2+}$, to which two perchlorate anions and two molecules of water are weakly coordinated. Two hydroxy groups are bridged between the two copper ions.

The compound was identified and characterized with the aid of chemical analyses, infrared spectra, ligand-field spectra, magnetic susceptibility, paramagnetic resonance spectra and conductivity measurements.

The magnetic measurements indicate antiferromagnetic character for the compound, with the spin singlet lying 175 ± 1 cm^{-1} below the spin triplet. A Neèl point was found at 159 ± 3°K.

Paramagnetic resonance spectra at X- and O-band frequencies yielded $g_x = 2.06 \pm 0.01$, $g_y = 2.05 \pm 0.01$ and $g_z = 2.26 \pm 0.01$; the axial zero-field splitting was found to be 0.72 ± 0.01 cm^{-1} with an additional rhombic splitting of 0.025 ± 0.005 cm^{-1}. The value for the axial splitting parameter is the largest thus far observed for binuclear Cu^{II} compounds.

Introduction

Many dimeric Cu^{II} compounds have been reported in literature. In these compounds the bridging groups usually are carboxylate[1-5] and oxo-ligands such as pyridine-*N*-oxides.[2,6-8] Also compounds with halide bridges are known.[2,9]

A few compounds of Cu^{II} are known to contain hidroxy groups as bridging ligands.[10-13] Terminal ligands in these complexes are *N,N,N',N'*-substituted ethylene diamines[10] and 2-substituted pyridines. The origin of the formation of the latter type of complexes seems to be the steric hindrance of the ligand substituents in the reaction with the small Cu^{II} ion.

Last year[14] indications were found that such dimers would occur for Cu^{II} and imidazole in aqueous solution.

We now wish to report the preparation and properties of the binuclear compound prepared from $Cu(ClO_4)_2$, 2-methylimidazole (2MIZ) and H_2O.

Experimental Section

Preparation of the Compound. Upon reaction between metal(II) perchlorates and tetrafluoroborates in ethanol, compounds of formula $M(2MIz)_4(anion)_2$ are found for many transition-metal ions.[15] With $Cu(ClO_4)_2$ however, no solid compound could be obtained by this procedure.

When this reaction is carried out in the presence of small amounts of water, a blue crystalline compound is obtained; this appears to be the title compound. The final synthesis of this compound was slightly modified to obtain a better yield.

2.0 g of $Cu(ClO_4)_2(H_2O)_6$ (0.55 mmole) was dissolved in 20 ml of ethanol. To this solution 2.0 g of triethylorthoformate (1.5 mmole) was added for partial-dehydration. Then 1.6 g of 2MIz (2.0 mmole) was added upon which the solution turned deep blue. Now 10 ml of chloroform was slowly added to the solution, after which it was allowed to evaporate slowly.

Dark blue crystals began to form within a few hours. When a small quantity of solvent rested, the crystals were collected on a glass funnel and washed with several portions of dry diethylether and finally

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dried *in vacuo* at room temperature. The yield was 1.5 g (80%). The compound melts at 150°C.

Analyses. The compound was analysed for copper (complexometric), nitrogen (Dumas), and carbon and hydrogen (carried out by Organisch Chemisch Instituut TNO, P.O. Box 5009, Utrecht). The results were: Cu, 17.37% (calcd 17.54); N, 15.40 (calcd 15.49); C, 26.77 (calcd 26.53); H, 4.27 (calcd 4.14).

Measurements. Infrared spectra in the range 4000-200 cm^{-1} were recorded as nujol mulls sandwiched betweed NaCl or polythene plates. Instruments used were a Unicam SP 1200 (4000-600 cm^{-1}) and a Hitachi EPI-L (700-200 cm^{-1}).

Ligand-field spectra were recorded on a Beckman DK-2A instrument, furnished with a reflectance attachment and a cryostate for low-temperature measurements.[16] The spectra were taken using magnesium oxide as a reference.

E.P.R.-spectra were recorded on Varian instruments at both X- and Q-band frequencies. Details of the performance of these instruments are given elsewhere.[17,18]

Magnetic susceptibilities were determined by the Gouy-metod in the range 100-300^0 K. The calibration of the instrument and the technique of the measurements have been reported previously[18].

The conductivity of the present compound was studied with a Philips cell, type GM 4221, on a conductivity bridge, type 4249. Acetone was used as a solvent. The measured conductivity for a 10^{-3} mol. solution of 225 ± 10 cm^2.Ω^{-1}.mol^{-1} agrees with an ionic form $[Cu_2(OH)_2(2MIz)_4]^{2+}2ClO_4^-$ in this solvent.

Characterization and Discussion

Infrared Spectra. The infrared spectrum of the title compound (hereafter called I) was compared with that of the free ligand and with those of the compounds $M(2MIz)_4(ClO_4)_2$. The spectra of these latter compounds will be described elsewhere.[15]

In fact all the bands that are present in the free ligand are also observed in the spectrum of I, just as found for the compounds $M(2MIz)_4(ClO_4)_2$. In addition, bands are observed at 3640 and 3610 cm^{1-} (sharp doublet), 1090 vs, 875 s, br, 622s, 469s, 410s, and 290 cm^{-1}. From these additional bands the strong ones at 1090 and 622 cm^{-1} are due to the ClO_4^- anion[15]. From the fact that these bands occur as rather sharp ones, and that no anion band occur at about 920 cm^{-1}, it may be concluded that the ClO_4 anion scarcely takes place in coordination, neither to the Cu^{II} ions, nor to the ligands (*via* hydrogen bonding).

The strong doublet near 3600 cm^{-1} can be assigned to the O—H stretching of the hydroxyl bridges[13,19,20]. The doublet character of this absorption indicates that the two O—H groups are not equivalent; this may be caused by many factors such as non-planarity of the dimeric unit or unequal hydrogen bonds with ligands or anions.[13]

The O—H stretchings of the water molecules in the compound are not observed as sharp absorptions, but presumably are hidden under the N—H stretching of the compound in the range 3100-3350 cm^{-1}.

The broad band at 875 cm^{-1} is tentatively assigned to an O—H deformation vibration.

The metal-nitrogen stretching vibration can be assigned in the region near 300 cm^{-1} for Cu^{II} compounds,[15] in accordance with the band in I near 290 cm^{-1}.

Finally, two strong bands at about 450 cm^{-1} have to be assigned. Following McWhinnie[13] these bands can be assigned to the symmetric and asymmetric Cu—O vibrations. The values in our compound are only slightly lower than those found for the bipy complexes.[13]

Ligand-field Spectra. To obtain information about the coordination polyhedron around the Cu^{II} ion, ligand-field spectra of I were recorded.

The observed band maximum at room temperature at 17.2 kK is in agreement with square-planar coordinated Cu^{II}.[21] Other dimeric hydroxybridged copper compounds have similar absorptions, *e.g.* 16.5-17.7 kK in complexes with 2-methylpyridine, 2-aminopyridine, and 2,2′-bipyridyl as the terminal ligands.[19] The exact position of this band is determined by the amount of the distortion and the ligand-field strength of the terminal ligands.[21]

Usually, such dimeric compounds also show an absorpion in the near-UV region.[2,12,19] Our compounds, however, only showed a weak shoulder near 26 kK, on a very intense UV charge-transfer band.

At liquid nitrogen temperature the band maximum of I in the visible region shifts to 17.6 kK, whereas the band shape does hardly alter. The shoulder on the UV band however, now becomes more pronounced and is observed at 26.6 kK. The assignment of this latter band is not clear and has been the suject of many investigations.[3,7,8,22,23]

Magnetic Susceptibility Measurements. The most convenient way of studying magnetic interactions between metal ions is the method of the magnetic susceptibility. This method yields rather accurate values of J, the exchange integral between the metal ions.[3-6,8,11,24] Usually the susceptibility data are fitted to the Bleany-Bowers equation:[25]

$$\chi_{corr} = \frac{2g^2N\beta^2}{kT} \times \frac{1}{3+\exp(-J/kT)} \qquad (1)$$

in which χ_{corr} is the molar susceptibility corrected for diamagnetism and for temperature independent paramagnetism. Later, Hyde *et al.*[6] introduced a correction term 0.448/T for monomeric impurities that

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might be present in small quantities and that influence dramatically the susceptibility at low temperatures.

Recently, Jotham and Kettle[4,26] introduced two modifications of formula (1), by taking one[26] or two[4] higher lying singlets into consideration, to account for metal-metal binding. With the aid of these alterations they obtained better agreement with experiment than previously.[26] Because of the fact that it makes hardly difference when one or two singlets are considered, we have chosen for the model with only one singlet above the triplet in the interpretation of our measurements.

So, the magnetic susceptibility of our present compound was studied in the range 100-300°K, and the results were fit by least squares to the equation:

$$\chi_{\mathrm{found}} = \chi_{(\mathrm{dia-tip})} + \frac{Y \times 0.445}{T} + (1-Y) \times \frac{2N\beta^2}{k} \times \frac{g^2}{T} \times 1/F \qquad (2)$$

in this formula $\chi_{(\mathrm{dia\text{-}tip})}$ stands for the diamagnetic correction and the temperature independent paramagnetism per two Cu ions.

Y = the fraction of monomeric impurity per 2 Cu.

g = the gyromagnetic ratio.

T = the temperature (°K).

F = $3+\exp(-J/kT)+\exp(-S/kT)$, in which J is the distance from the ground-state singlet to the triplet, and S is the distance from the triplet to the higher singlet.

In the least-squares procedure $\chi_{(\mathrm{dia\text{-}tip})}$, Y, g, J, and S were refined. The final values are listed in Table I, together with the experimental and calculated values for the susceptibility at the several temperatures.

The correction term for the diamagnetism and the temperature independent paramagnetism obtained in this way, agrees very well with that calculated from Pascal's constants[27] (yielding $\chi_{\mathrm{dia}} = -34 \times 10^{-5}$ c.g.s. units), and the expression for TIP:[28] $\chi_{\mathrm{tip}} = 2 \times 4N\beta^2/10Dq$ (yielding 11×10^{-5} c.g.s. units).

Table I. Magnetic susceptibility data and calculated parameters of I

Temperature (°K)	χ_{found} [a]	χ_{calc} [a]	Parameters
293	188	185	$\chi_{\mathrm{dia\text{-}tip}} = -24 \pm 1 \times 10^{-5}$
253	206	204	$g = 2.118 \pm 0.005$
213	223	222	$J = -175 \pm 1$ cm^{-1}
193	230	230	$Y = 0.020 \pm 0.005$
173	235	237	$S = -1100 \pm 200$ cm^{-1}
164	236	238	
159	237	238	
154	236	238	
145	235	237	
136	233	234	
127	227	228	
118	218	219	
109	210	207	
100	194	189	

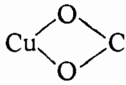
[a] χ value are in c.g.s. units $\times 10^{-5}$.

The observed g-value agrees very well with the averaged value from the EPR-spectra (to be described below); the difference is well within experimental uncertainties.

The S-value obtained by the least-squares procedure is rather inaccurate because of its magnitude; a variation of 10% in this parameter influenced the susceptibility only by 0.5×10^{-5} c.g.s. units, whereas the experimental uncertainty amounts to $1\text{-}2 \times 10^{-5}$ units. The only comparable literature values for S are those of the Cu$^{\mathrm{II}}$-carboxylates, that are somewhat smaller. This in fact indicates that direct metal-to-metal bonding is less important than in the carboxylate dimers.[26]

The magnitude of Y indicates that 2% of the compound is monomeric rather than dimeric; this means that per Cu atom 1% monomer occurs. EPR-spectra also indicate an amount of monomeric species of this order (see below).

The J-value of our compound of −175 cm^{-1} is rather small compared with literature values. Carboxylate compounds of Cu usually have J values in the range −125 cm^{-1} (Cu-α-naphtoate[5]) to −445 cm^{-1} (Cu$^{\mathrm{II}}$formate-monopyridine[4]), whereas *N*-oxide compounds[6] have J values from −550 to −885 cm^{-1}. Values available for hydroxy-bridged compounds similar to I, with general formula $[\mathrm{Cu(OH)(ligand)_2}]_2^{2+}(\mathrm{anion})_2^{-}$, are: −509 cm^{-1} for *N,N,N',N'*-tetramethylenediamine as the ligand and $\mathrm{Br^-}$ as the anion,[24] −410 cm^{-1} for *N,N*-diethyl-*N'*-methylethylenediamine as the ligand and perchlorate anions,[11] −375 cm^{-1} for *N,N,-N',N'*-tetraethylethylenediamine as the ligand and perchlorate as the anion,[11] −175 cm^{-1} for 2-methylimidazole (present work). A positive J value of 48 cm^{-1} has recently been reported[29] for $[\mathrm{Cu(OH)(bipy)_2}]_2\mathrm{SO_4} \cdot 5\mathrm{H_2O}$; i nthis compound $\mathrm{CuO_2Cu}$ moiety however is not planar.

There might be a relation between the planarity of the dimeric unit  and the magnitude of J; (Cf. the stricktly planar unit[24] having J = −509 cm^{-1} and the rather bend unit[29] having J = +48 cm^{-1}). However, because of the fact that no X-ray structural information is available for the intermediate compounds, further conclusions about this subject are not allowed.

Electron Paramagnetic Resonance Spectra. The rather small value of J and the fact that considerable paramagnetism occurs at room temperature, allowed us to study the paramagnetic resonance spectrum of the thermal populated triplet state.

Such triplet spectra are well known for organic triplet molecules,[30] for $\mathrm{Ni^{2+}}$ (high spin),[18,31] and also for some copper(II) dimers.[5,7,32] The parameters that can be evaluated from these spectra are the g tensors, the axial zero-field splitting, (D), and the rhombic splitting, (E), of the triplet state.

It seemed interesting to study the paramagnetic

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behaviour of our compound, to calculate the zero-field splittings, and to compare the averaged g-value with that of the susceptibility measurements.

Initial X-band resonance measurements (9.5 GHz) showed four rather broad bands of the triplet species apart of some monomeric impurity near $g = 2.1$ (of the order of 1%). These broad bands were unsufficient to calculate accurate parameters. Therefore, spectra were also recorded at Q-band frequency (35 GHz). Now seven lines were observed that allowed calculation of the parameters g_x, g_y, g_z, D and E (or λ being E/D).

The equations used to obtain the parameters, were those listed by Wasserman *et al.*[30] and Wasson *et al.*[32] for the $\Delta m = \pm 1$ transitions. In addition, two other transitions are observed when $D < 3/4\ h\nu$; these are the double-quantum transition, H_{dq}, and the $\Delta m = \pm 2$ transition (H_{min}). For these transitions, the following equations hold:

$$H_{dq} = \frac{2}{g_{av}} \times [H_o^2 - (\frac{1}{3}D^2 + E^2)]^{1/2} \qquad (3)$$

in which:

$$g_{av} = [\frac{g_x^2}{3} + \frac{g_y^2}{3} + \frac{g_z^2}{3}]^{1/2} \qquad (4)$$

and

$$H_{min} = \frac{2}{g_{min}} \times [\frac{H_o^2}{4} - (\frac{1}{3}D^2 + E^2)]^{1/2} \qquad (5)$$

in which:

$$g_{min} = [\sin^2 a \times g_\perp^2 + \cos^2 a \times g_z^2]^{1/2} \qquad (6)$$

$$\text{with } g_\perp = (g_x \cdot g_y)^{1/2} \text{ and } \cos^2 a = \frac{9-4(D/h\nu)^2}{27-36(D/h\nu)^2} \qquad (7)$$

Equation (7) has been derived from the calculations of de Groot and van der Waals,[33] after setting E to zero, and determining that value of $\cos^2 a$ for which $g\beta H/h\nu$ reaches a minimum as a function of $D/h\nu$, and cos a.

When D-values are large, X-band spectra usually yield rather broad bands,[18,31,34] but Q-band spectra yield sharp bands for H_{dq} (only when $D/h\nu < 1.73$) and H_{min} (only when $D/h\nu < 0.75$),[18] so that these resonance fields are easiest assigned. For the present compound we obtained a rough value for D from these two bands.

To obtain the parameters g_x, g_y, g_z, D and E from the observed X- and Q-band spectra, we used computer produced graphs with $H_{res}/h\nu$ plotted against $D/h\nu$. In these graphs the observed resonance fields were tried to fit (after dividing through $h\nu$) for both frequencies. In this way rough values for the parameters were obtained, which were refined by least-squares procedures to a best fit with all the observed band maxima (8 Q-band and 4 X-band resonances), giving the heaviest weights to the sharpest lines. The final graph is presented in Figure 1. The calculated $D/h\nu$ values for both X- and Q-band frequencies are indicated by dashed lines. Resonance fields for our compound are observed at the crossings of the resonance lines with the dashed lines. The exact band maxima (calculated and observed) are listed in Table II, together with the assignments, and the final parameters.

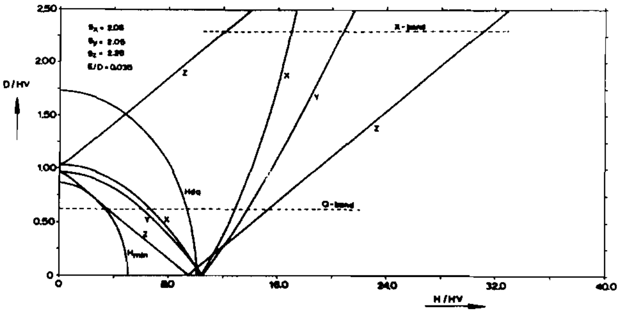

Figure 1. Predicted EPR-transitions as a function of $D/h\nu$, for given values of the g-tensors and E/D; the dashed lines indicate the resonance absorptions for I at X- and Q-band frequencies.

The magnitude of the g-values is in the range usually found for tetragonal Cu^{II} compounds with nitrogen-donor ligands.[21] The fact that g_x and g_y differ very little can be explained by the (pseudo-) tetragonal symmetry. The value of 2.26 for g_z has been found for many other compounds with imidazoles.[35] The averaged gyromagnetic ratio, g_{av}, of 2.120 is very close to that found from the magnetic susceptibility measurements.

The observed D value of our compound is the largest value thus far reported for binuclear Cu^{II} compounds. Some literature values are 0.35-0.39 cm^{-1} for Cu^{II} carboxylates,[5] 0.15-0.21 cm^{-1} for pyridine-*N*-oxide compounds,[7] 0.06-0.12 cm^{-1} for Cu^{II} tartric acid[36] and adenine complexes, and 0.035 cm^{-1} for $Cu_2(dimethylglyoxim)_4$.[37]

Usually, the contributions to the experimental D value are assumed to be a dipole-dipole interaction between the unpaired electrons, D_{dd}, and a pseudo-dipolar term (originating in spin-orbit coupling), D_{psd}, for which holds:

$$D_{exp} = D_{dd} + D_{psd} \qquad (8)$$

For both of these terms theoretical expressions are known, *i.e.*[36]

$$D_{dd} = 0.65 \times g_z^2/R^3 \qquad (9),$$

in which R is the averaged distance between the two electrons, usually taken as the Cu–Cu internuclear distance; and:[25]

$$D_{psd} = -1/8[J_1(g_z-2)^2/4 - J_2(g_\perp-2)^2] \qquad (10)$$

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Table II. Comparison of experimental and calculated EPR-bands, and the calculated parameters (room temperature).

Frequency range	Observed [a] bands	Calculated [a] bands	Assignment	Parameters [b]
X-band	3800±200	3806	HZ_1	$g_x=2.06 \pm 0.01$
(9521 GHz)	5300±100	5408	HX_2	$g_y=2.05 \pm 0.01$
	6500±100	6534	HY_2	$g_z=2.26 \pm 0.01$
	9700±200	9831	HZ_2	
Q-band	3975±10	3979	H_{min}	$D=0.72 \pm 0.01$
(34,780 GHz)	4100±200 [c]	4165	HZ_1	$E=0.025 \pm 0.005$
	7100±100	7090	HY_1	$\lambda=0.035 \pm 0.005$
	7850±100	7804	HX_1	
	10915±15	10912	H_{dq}	
	14900±100	14918	HX_2	
	15800±100	15868	HY_2	
	17800±100	17818	HZ_2	

[a] Bands are in Gauss; [b] D and E are in cm^{-1}; [c] HZ_1 is hidden under the H_{min} absorption.

in which J_1 and J_2 are the exchange terms for $d_{x^2-y^2}$ with d_{xy}, and for $d_{x^2-y^2}$ with d_{xz}/d_{yz} respectively.

Taking R equal to 2.9 Å (Cu–Cu distances in such compounds vary from 3.0 Å[10,38] to 2.8 Å[39-41]), and $J_1=J_2=J_{susc.}$ ($J_{susc.}$ obtained from Table I), equations (9) and (10) yield: D_{dd} = 0.14 cm^{-1} and D_{psd} = 0.30 cm^{-1}. The sum of these two terms (0.44 cm^{-1}) is considerably smaller than the experimental D of 0.72 cm^{-1}. However, several approximations in equations (9) and (10) invalidate the use of such calculations. These are the unknown electron-electron distance in the point-dipole model; although most workers use the experimental Cu–Cu distance, this may be incorrect and electron delocalization (covalency) certainly will influence R. A 20% smaller R value for instance yields D_{dd} = 0.24 cm^{-1}. Further, the values of J_1 and J_2 need not necesseraly to be equal to the susceptibility value; much smaller values or much larger ones may occur.[7,25] Finally their may be non-coincidence between the g and the D principal directions, that also influence equations (9) and (10).

The observed E value of our compound is rather small and indicates a small distortion from axial symmetry, in agreement with the small difference between g_x and g_y.

Conclusion

The present investigations have shown that the compound $Cu(OH)(2MIz)_2(ClO_4)_2(H_2O)_2$ consists of dimeric hydroxy-bridged Cu^{II} pairs with an antiferromagnetic interaction (J = −175 cm^{-1}) between them. The perchlorate anions and the water ligands seem to be only weakly coordinated to the Cu^{II} ions, yielding a nearly square-planar CuN_2O_2 species for each half of the dimer.

The origin of the large zero-field splitting of the spin triplet state of the compound is not understood at the moment; direct dipole-dipole and pseudo-dipolar interactions between the unpaired electrons yield too small values.

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