Pressure-Induced Temperature Dependence of a Weak Exchange Coupling in Dichlorobis(1-phenyl-3,5-dimethylpyrazole)copper(II) Crystals

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X-band EPR temperature and pressure (up to 450 MPa) measurements of the dichlorobis(1-phenyl-3,5-dimethylpyrazole)copper(II) crystal show that exchange coupling between Cu(II) ions is very weak with $|J| = 0.003\ 86\ \mathrm{cm}^{-1}$ at room temperature. This coupling is temperature independent but decreases under pressure. Moreover, when pressure is applied to the crystal, the J-value becomes temperature dependent and decreases on cooling. Also the g_z-factor and the line width value are affected by temperature and pressure. These effects are discussed and explained as a result of a decrease of the tilt angle between the pyrazole ring and Cu(II) coordination plane under pressure and a shortening of the Cu-N bond on cooling. Exchange coupling is suggested to be ferromagnetic at normal conditions with an antiferromagnetic contribution appearing under pressure.

Introduction

EPR spectra of condensed paramagnets are obscured by exchange coupling between paramagnetic ions. When exchange coupling is not much stronger than splitting between EPR lines, i.e. of about 0.1 cm^{-1}, some effects from individual centers can appear. The individual lines are still not resolved, but the line width value and its angular dependence are governed, to some extent, by the merging effect between the lines. When the exchange integral is comparable to some critical J_{cr}-value, the spectral lines become resolved, at least at some crystal orientations.[1] It allows one to perform a computer simulation of the lines and to determine, with high accuracy, an exchange integral value in a range from 10^{-4} to 10^{-1} cm^{-1} depending on the line width value.[2,3] For all copper(II) crystals with weak exchange coupling that have been studied so far it has been found that the coupling between dimers, chains, and individual complexes is temperature and pressure dependent.[2-6] Unexpectedly during EPR anisotropy studies of single crystals of dichlorobis(1-phenyl-3,5-dimethylpyrazole)copper(II) ≡ Cu(pdmp)$_2$Cl$_2$ we have found that the weak exchange coupling $|J| = 0.003\ 86\ \mathrm{cm}^{-1}$ is temperature independent.[7] This observation came as a surprise since a small exchange is a result of a delicate balance between statical and dynamical contributions affecting superexchange transmission through extended atomic pathways.

However, when hydrostatic pressure was applied to the crystal, we found that the J-value decreased, and moreover a temperature dependence of the J-value appeared. These results will be discussed in the present paper.

The monoclinic Cu(pdmp)$_2$Cl$_2$ = $\mathrm{CuCl_2C_{22}H_{24}N_4}$ crystal contains two magnetically inequivalent molecules per unit cell.[8] The molecules are arranged in a two-dimensional network parallel to the *bc* crystal plane. Copper(II) ions are coordinated by two chlorides and two nitrogens in an exactly planar trans-configuration (Figure 1).

Computer simulations of the two-line spectra in EPR angular dependence studies gave the following molecular g-factors of individual Cu(II) complexes: $g_x = 2.036$, $g_y = 2.050$, and $g_z = 2.230$, with the x-axis along the Cu-N direction and the y-axis along the Cu-Cl bond, and an angle of 140.4° between the z-axes of inequivalent centers.[7] Low values of the perpendicular g-factors, especially g_x, are explained as a result of a strong delocalization of the unpaired electron onto ligands both in the x^2-y^2 ground state and excited states. The g_x and g_y values are approximately temperature independent whereas the g_z value clearly decreases on cooling. We conclude that this can be associated with a fluxional behavior of the Cu(II) complexes with inequivalent ligands.[9]

Experimental Section

Dichlorobis(1-phenyl-3,5-dimethylpyrazole)copper(II) single crystals were obtained by reaction of the metal salt and ligand in ethanol and recrystallized from ethanol. The dark green crystals form rods which are elongated along the [101] direction with well-developed (111) and (101) planes. EPR spectra were recorded on a Radiopan SE/X-2542 spectrometer equipped with a high-pressure (up to 450 MPa) beryllium-bronze chamber with a cylindrical corundum TE$_{112}$ resonator and at 80-Hz magnetic modulation.[10] A single crystal was mounted in the resonator and surrounded by petroleum ether as a hydrostatic pressure transmitter. Crystals were oriented in the orthogonal 1, 2, 3 reference frame related to the crystal habit with axis 1 perpendicular to the $(11\bar{1})$-plane and axis 3 along the [101] direction.

Results and Discussion

Pressure and temperature EPR measurements were performed for a single crystal at an orientation where the two lines in the spectrum were well resolved, i.e. in the 3,1-plane at $\theta = 135°$. The spectra recorded in this orientation under different conditions are shown in Figure 2 together with computer-fitted spectra obtained with $|J| = 0.003\ 86\ \mathrm{cm}^{-1}$ at room temperature and $|J| = 0.000\ 90\ \mathrm{cm}^{-1}$ at 77 K and 450 MPa.

Temperature and pressure variations of the exchange integral $|J|$ are shown in Figure 3. The exchange coupling is temperature independent under a normal pressure of 0.1 MPa, but under hydrostatic pressure the $|J|$-value decreases. Moreover, under

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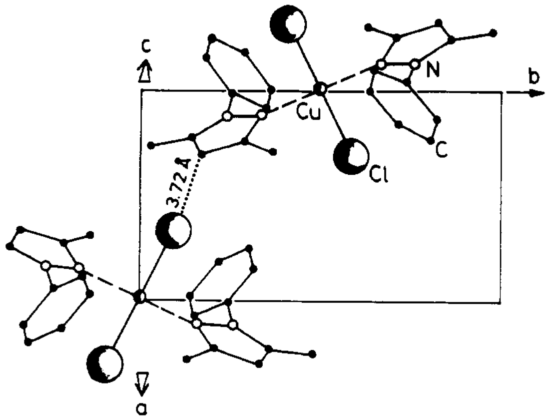

Figure 1. Projection of the crystal structure along the [201] direction. Only two nonequivalent complexes are shown.

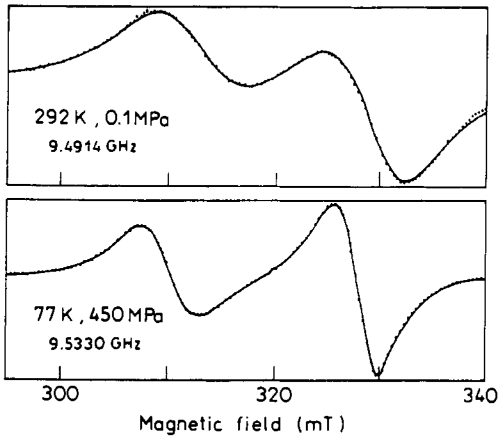

Figure 2. Experimental spectra (points) recorded at different conditions in the 3,1-plane, $\theta = 135°$, and theoretical computer-fitted spectra (solid lines) with exchange integral $|J| = 0.003\,86$ cm^{-1} at 292 K and $|J| = 0.000\,90$ cm^{-1} at 77 K. The experimental spectra were obtained with 0.2-mT modulation amplitude and 23-mW microwave power.

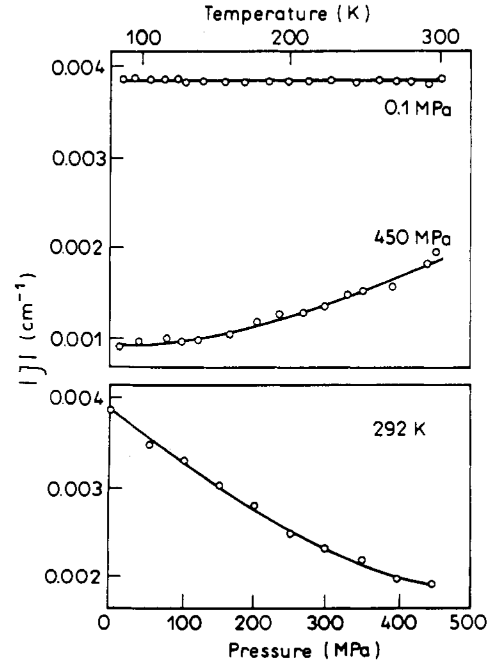

Figure 3. Temperature and pressure dependence of the exchange integral $|J|$ in the Cu(pdmp)$_2$Cl$_2$ crystal. The solid lines are guides for the eye.

pressure a $J(T)$ dependence appears and the $|J|$-value decreases with temperature. Thus, the pressure forces such changes in the crystal structure that exchange coupling becomes temperature sensitive, a phenomenon that is commonly observed in Cu(II) compounds.

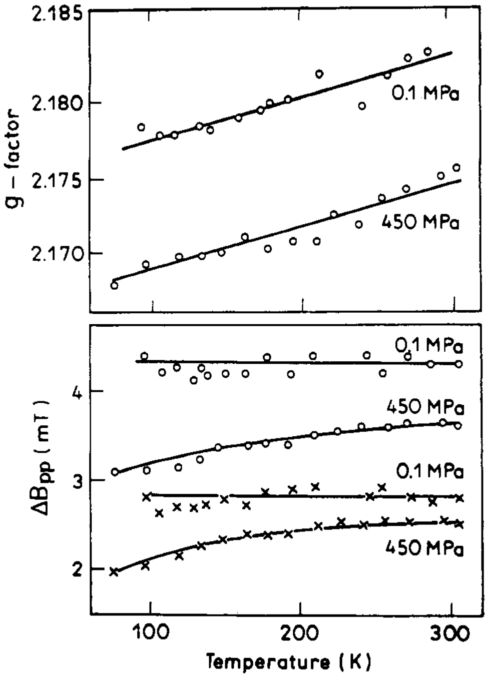

Figure 4. Temperature dependence of the g-factor and the line width value ΔB_{pp} under normal and high pressure measured in the 3,1 plane, $\theta = 135°$. The open circles indicate the low-field line, and the crosses indicate the high-field line. The g-factor of the high-field line is temperature independent; $g = 2.078(2)$. The solid lines are guides for the eye.

In this crystal, an increase in pressure affects the exchange coupling in the same manner as a decrease of temperature. This is behavior that is observed when thermal expansion of a crystal lattice dominates lattice vibrational effects in the temperature dependence of a physical parameter. However the pressure effect is larger than the temperature effect in our crystal, which is rarely the case, and indicates a large or strongly anisotropic compressibility of the crystal as compared to the crystal lattice expansion. The observed $J(T)$ and $J(p)$ dependencies with $(dJ/dT)_p > 0$ and $(dJ/dp)_T < 0$ are atypical with similar behavior being reported only for the M(en)$_3$CuCl$_5$·H$_2$O (M = Co, Rh, Ir) family.[2] Typically $|J|$ increases on cooling and under pressure.

The J-value behavior in Cu(pdmp)$_2$Cl$_2$ can be phenomenologically explained in terms of the model described in ref 11. In this model an effective exchange coupling $|J|$ measured by EPR is the sum of two components: a positive ferromagnetic contribution J_F, which is practically temperature independent, and a negative antiferromagnetic contribution J_{AF}, which is temperature sensitive and increases on cooling as a result of a thermal lattice contraction. We assume that in the Cu(pdmp)$_2$Cl$_2$ crystal at normal pressure the exchange coupling is ferromagnetic in origin ($|J| = J_F$) so it is not affected by temperature. The pressure induces an antiferromagnetic contribution which increases on cooling and continuously diminishes the effective exchange coupling $|J| = J_F + J_{AF}(T)$. Thus Cu(pdmp)$_2$Cl$_2$ belongs to the minority of copper(II) compounds with ferromagnetic coupling between Cu(II) ions.

The exchange interaction described above is a coupling between inequivalent Cu(II) sites which give resolved lines in the EPR spectrum. There is no through-bond exchange pathway between two Cu(II) sites in the crystal structure (Figure 1). We propose that the superexchange may be transmitted through the pyrazole ring to the Cl atom of a neighboring Cu(II) complex since this

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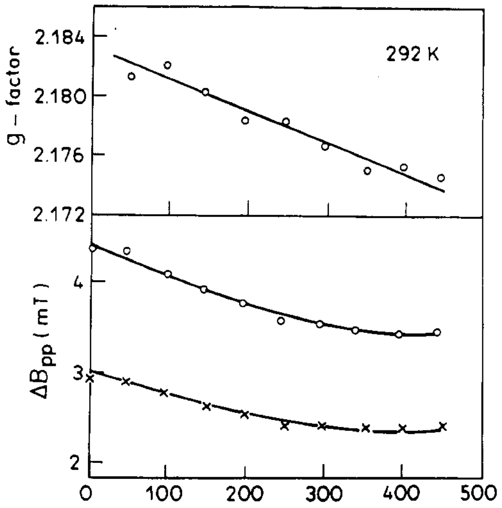

Figure 5. Pressure dependence of the g-factor and the line width value ΔB_{pp} at 292 K for the low-field line (circles) and high-field line (crosses). The solid lines are guides for the eye. The g-factor of the high-field line is pressure independent.

is a closest physical contact between the sites. This distance is rather long (3.72 Å), however, and C–H···Cl hydrogen bond formation, although less probable, cannot be ruled out. Another possibility is that there may exist a direct through-space exchange interaction between Cu(II) ions, and this would be expected to be ferromagnetic.

Additional information is given by the temperature and pressure dependencies of the g-factor and line width value ΔB_{pp}. These data are presented in Figures 4 and 5. The g-factor measured near the z-axis is affected by temperature and pressure, whereas the perpendicular g-factors are essentially not affected. The ΔB_{pp} value behavior is similar to that of the $|J|$ value—it depends on pressure but is not affected by temperature at 0.1 MPa. However, the $\Delta B_{pp}(T)$ dependence appears when hydrostatic pressure is applied to the crystal.

The observed temperature and pressure effects in the crystal can be rationalized in terms of (a) a decrease of the tilt angle of the Cu(II) complexes under pressure and (b) temperature-dependent influences on the length of the Cu–N bond. These two mechanisms have been postulated to operate in Cu(II) complexes with heterocyclic rings.[12,13]

It is known that when the nitrogen atom of the aromatic ring is coordinated to Cu(II), superexchange transmission through the ring depends primarily on the degree of tilting of the ring with respect to the Cu(II) main coordination plane.[12,14] When the angle is equal $\pi/2$, the $x^2 - y^2$ ground state is perpendicular to the aromatic ring and a weak ferromagnetic coupling is expected. When the ring is coplanar with the Cu(II) coordination plane, the antiferromagnetic contribution will dominate. Thus, an increase in J_{AF} is expected when the tilt angle decreases due to the increase in delocalization of the unpaired electron onto the aromatic ligand.

The tilt angle is equal to 79.8° in $Cu(pdmp)_2Cl_2$ at normal conditions. This angle decreases under pressure, since a larger crystal compressibility is expected in the direction perpendicular to the crystal layers than in the *bc*-planes. As a result, a J_{AF} contribution to J_{eff} appears and $|J_{AF}|$ increases with pressure.

This increase in the delocalization of the unpaired electron onto the ligand and the decrease in the tilt angle results in (a) a decrease in g_z-value due to lowering of α^2 and β^2 MO coefficients in the relation $g_z = 2 - 8\lambda\alpha^2\beta^2/E_{xy}$ and, (b) a decrease in hyperfine splitting A_z which is reduced by the α^2-coefficient. The latter effect is observed by the narrowing of the EPR lines under pressure, since the line width value is determined mainly by nonresolved hyperfine structure.

Temperature does not influence the tilt angle value, since the average complex geometry is vibrational independent. However, the observed decrease of g_z on cooling with a constant line width value indicates that the E_{xy} value increases but α^2 is not affected. This is a result of a small shortening of the Cu–N bond when the amplitude of molecular vibrations decreases. A similar effect was observed as a result of the steric requirements of the substituents on the pyrazine ring.[12] The $g_z(T)$ and $A_z(T)$ dependencies under pressure are driven by the $\alpha^2(T)$ dependence which appears in the pressure-deformed asymmetrical complex.

The mechanism by which the exchange interaction is transmitted in the $Cu(pdmp)_2Cl_2$ crystal is not known. We were able, however, to identify the main molecular factors which affect the J-value and the EPR parameters. These factors are the decrease in the tilt angle under pressure and the shortening of the Cu–N bond on cooling.

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