Ferromagnetic Interactions in Dimeric Dichloro-[2,2-bis-(2-pyridyl)-1,3-dioxolane]copper(II)

CHARLES J. O'CONNOR

Department of Chemistry, University of New Orleans, New Orleans, La. 70148, U.S.A.

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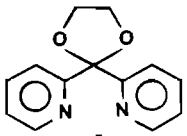
Newkome and coworkers have recently reported some unusual divalent transition metal complexes of Co, Ni, and Cu prepared from 2,2-bis-(2-pyridyl)-1,3-dioxolane (**L**) [1–3]. In addition, a complex of **L** with palladium has also been reported by Annibale and coworkers [4].



L

It has been shown that **L** acts as a tridentate ligand that binds to the metal via the two pyridyl nitrogens as well as one of the oxygens of the five membered ring. In the $CuLCl_2$ complex, the copper(II) ion is also coordinated by the two chloride anions giving a five coordinate monomer with square pyramidal geometry. A sixth axial coordination position is occupied by a chlorine from a neighboring molecule, resulting in a weak dimer formation of $[CuLCl_2]_2$. The structure of the molecule is illustrated in Fig. 1.

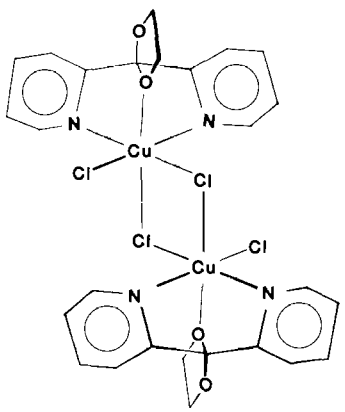


Fig. 1. Structural diagram of the binuclear unit $[CuLCl_2]_2$.

As noted by Newkome and coworkers [1], our preliminary analysis of this molecule over the 15–300 K temperature region did not reveal the presence of an appreciable magnetic coupling. We have since measured the magnetic susceptibility of the complex at a lower temperature (2–300 K), and report here on the ferromagnetic interactions that we have observed at lower temperature.

Experimental

The magnetic susceptibility of a 100 mg sample of $CuCl_2C_{13}H_{12}N_2O_2$ was measured over the 2–300 K temperature range at measuring field of $H = 1.0$ k0e with the SHE Corporation model VTS-50 superconducting susceptometer. Measurement and calibration techniques are described elsewhere [5].

Results and Discussion

The magnetic data are illustrated in Fig. 2 with a plot of the effective magnetic moment ($\mu_{eff} = \sqrt{7.997\chi T}$) as a function of temperature. A constant moment over most of the temperature range is consistent with Curie–Weiss law as shown in eqn. (1).

$$\chi = \frac{Ng^2\mu_B^2 S(S+1)}{3k(T-\theta)} + TIP \qquad (1)$$

where $S = 1/2$ for copper(II), TIP is the temperature independent paramagnetism, and all of the other parameters have their usual meaning. The data were analyzed with eqn. (1) and the best fitted parameters are $g = 2.12$, $\theta = 1.0$ K, and $TIP = 20 \times 10^{-6}$ emu/g-atom Cu. The positive value for theta and the increase of the effective moment at low temperature indicate that there is a ferromagnetic interaction within the dimeric unit.

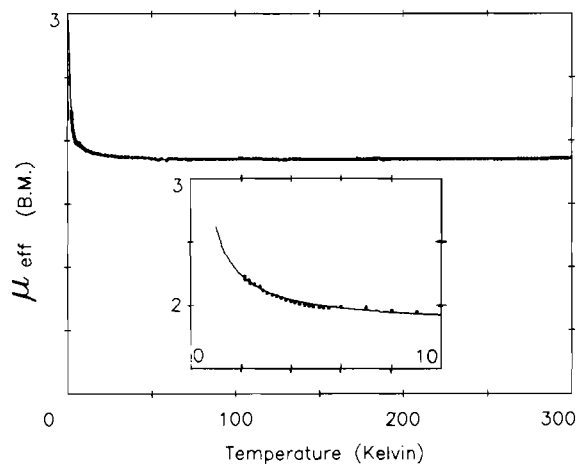


Fig. 2. Plot of the effective magnetic moment as a function of temperature for $[CuLCl_2]_2$. The curve drawn through the points is the best fit of the magnetic data to the binuclear equation as described in the text.

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The magnetic behavior of a copper(II) dimer is expected to follow the Bleaney–Bowers equation [6]

$$\chi = \frac{Ng^2\mu_B^2}{kT} \frac{e^x}{1+3e^x} + TIP \quad (2)$$

where $x = 2J/kT$ and $2J$ is the singlet triplet splitting with a positive J having a ground triplet.

To adequately fit the magnetic data, it was necessary to correct the intradimer magnetic susceptibility (eqn. (2)) for an interdimer exchange interaction using eqn. (3) [5].

$$\chi' = \frac{\chi}{1 - (2zJ'/Ng^2\mu_B^2)\chi} \quad (3)$$

where χ' represents the susceptibility actually measured, χ is the susceptibility calculated from eqn. (2), and zJ' is the exchange between the neighboring dimeric units. The best fit of the magnetic data using eqns. (2) and (3) is illustrated in Fig. 2 by the smooth line drawn through data points. The fitted values are $g = 2.12$, $J/k = 3.5$ K, $zJ'/k = 0.55$ K, and $TIP = 25 \times 10^{-6}$ emu/g-atom Cu.

There has recently been a great deal of interest in magneto–structural correlations in exchange coupled systems. The magnitude of the magnetic exchange of hydroxide bridged complexes was shown to exhibit a linear relationship with the bridging angle ϕ(Cu–O–Cu) [7]. More recently it has been shown that the magnetic exchange for chlorine bridged copper dimers follows a more complex behavior. The magnitude of the magnetic exchange shows a dependence on the combination of the bridge angle ϕ(Cu–Cl–Cu) and the long (axial) Cu–Cl bond [8]. Hatfield has empirically shown that the magnetic exchange for chlorine bridged copper dimers depends on the ratio ϕ/r.

The angle ϕ for the Cu–Cl–Cu bridge is 96.68° and the bridging distances are $Cu–Cl_{(b)}$(axial) = 2.844 and $Cu–Cl_{(eq)}$ = 2.273 Å for the long and short bonds of the bridge. The Cu–Cu separation is 3.8417 Å. Hatfield has tabulated the properties of several of the copper(II) dimers in which the bridging plane is perpendicular to the copper(II) tetragonal plane. In chlorine bridged copper(II) dimers of this type, values of ϕ/r between 31.0 and 34.5 will exhibit ferromagnetic interactions. For the complex reported here, ϕ/r = 34.0, which falls in the ferromagnetic range. The magneto–structural parameters of this complex agree very well with the empirical correlation of Hatfield.

Acknowledgements

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