*Inorganica Chimica Acta,* 36 (1979) L419–L420

# Single Crystal ESR Spectra of a Heterodinuclear Copper(II)–Nickel(II) Tetra-Schiff Base Macrocyclic Complex

L. BANCI, A. BENCINI, D. GATTESCHI

*Istituto di Chimica Generale ed Inorganica dell'Università di Firenze; Laboratorio C.N.R.; Via Jacopo Nardi 39, 50132 Florence, Italy*

and A. DEI

*Istituto di Chimica Generale ed Inorganica della Facoltà di Farmacia, Università di Firenze, Via Gino Capponi 7, 50123 Florence, Italy*

Received June 2, 1979

In recent years the superexchange interactions between metal ions have been thoroughly examined [1]. Although the nature of the interactions is reasonably well understood in the case of polynuclear complexes formed by identical metal ions, far less numerous reports are available for the case of complexes formed by different metal ions [2]. We have recently reported the magnetic resonance spectra of some heterodinuclear complexes of weakly coupled metal ions [3], for which the ESR resonances of one ion are not substantially affected by the other metal ion, and we wish now to report the ESR spectra of a strongly coupled copper(II)–nickel(II) complex in which only the resonance due to the couple could be observed.

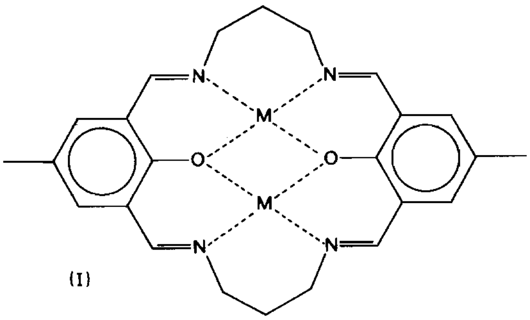
Recently a series of dinuclear metal(II) complexes of a tetra-Schiff base macrocycle, formed as condensation product of propane-1,3-diamine and 2-hydroxy-5-methylisophthaldehyde (I), has been reported [4].

The X-ray crystal structure of the dichlorodicopper(II) derivative [5] has shown that each metal ion is coordinated by four donors of the macrocyclic ligand and a halogen atom in a square pyramidal geometry, according to scheme (II). The magnetic properties of this complex showed that the two copper(II) ions are strongly antiferromagnetically coupled, the magnetic moment at room temperature being 0.6 $\mu_B$ [4].

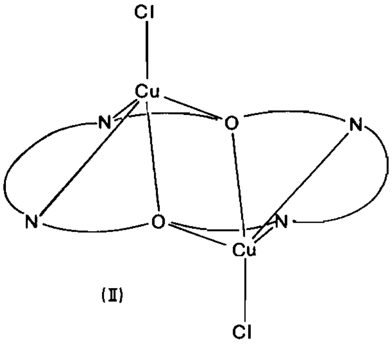
We doped this complex with 1% nickel(II) and 1% zinc(II) and recorded the ESR spectra at 4.2 K. Due to the high value of J, the host lattice is diamagnetic well above liquid helium temperature.

The polycrystalline powder ESR spectra of the zinc(II) doped complex are normal copper(II) spectra with $g_\parallel = 2.24, g_\perp = 2.06, A_\parallel = 178 \times 10^{-4}$ cm$^{-1}$.

The polycrystalline powder ESR spectra of the nickel(II) doped complex are shown in Fig. 1. They are not readily interpreted since several features are observed. In the single crystal spectra however, two sets of signals are observed. Their relative intensities vary from crystal to crystal. We assume that one of these sets is due to the copper(II)–nickel(II) complex (Cu–Ni), while the other is due to some complex containing one single copper(II) ion (Cu).



(I)



(II)

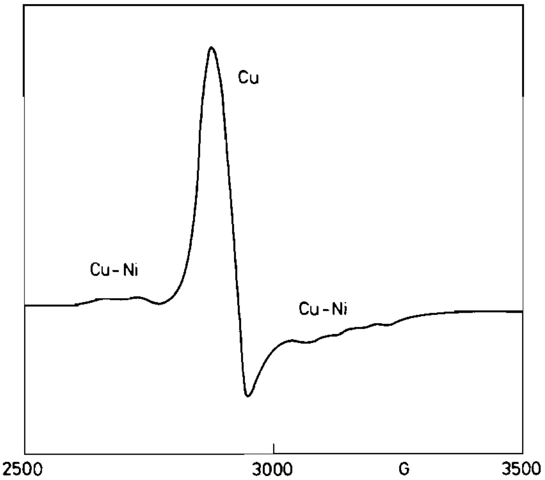


Fig. 1. Polycrystalline powder ESR spectrum of 1% Ni doped $Cu_2LCl_2$ at 4.2 K.

Since the crystals are monoclinic and the dimers possess $C_2$ symmetry [5], one principal $g$ value is found parallel to $b$, $g_2 = 2.41$ for the Cu–Ni complex and $g_2 = 2.05$ for the Cu one. The second principal $g$

value is found to be approximately orthogonal to the macrocyclic plane, $g_1 = 2.09$ for the Cu–Ni and $g_1 = 2.22$ for the Cu complex. In correspondence to these $g$ values a hyperfine splitting is also resolved, being $49 \times 10^{-4}$ cm$^{-1}$ for the Cu–Ni complex and $192 \times 10^{-4}$ cm$^{-1}$ for the Cu one. The third principal $g$ values are $g_3 = 2.49$ and $g_3 = 2.08$ for the Cu–Ni and Cu respectively. No hyperfine structure was resolved in correspondence of both $g_2$ and $g_3$.

The $g$ and $A$ values for the Cu complex are normal for tetragonal copper(II) complexes, perhaps closer to the square planar than to the square pyramidal limit [6].

The $g$ and $A$ values for the Cu–Ni complex can be compared to the values obtained by Kokoszka for the nickel(II) doped dichloroaquo(pyridine-N-oxide)-copper(II) complex [7] ($g_1 = 2.14$, $g_2 = 2.49$, $g_3 = 2.54$, $A_1 = 35 \times 10^{-4}$ cm$^{-1}$), which he considered to be due to copper(II)–nickel(II) couple. The $A_1$ value observed by us for the Cu–Ni complex is close to one third of the value found for the zinc(II) doped complex, as one would expect for a copper(II)–nickel(II) couple [8].

The $g$ values of the Cu–Ni complex can be considered related to the $g$ values of the corresponding Cu and Ni monomeric complexes according to the relation

$$g = \frac{1}{2}(g_{Cu} - g_{Ni}) - \frac{5}{6}(g_{Cu} - g_{Ni})$$

The $g_{Cu}$ values can be guessed from the values of the zinc(II) doped complex. With these values it is found $g_{1,Ni} = 2.12$, $g_{2,Ni} = 2.32$, $g_{3,Ni} = 2.38$.

A full characterization of the temperature dependence of the ESR signals is under way to evaluate the copper(II)–nickel(II) magnetic coupling constant, together with a complete theoretical treatment, using both spin Hamiltonian and angular overlap formulism.

## Acknowledgment

Thanks are due to Prof. L. Sacconi for encouragement.

## References

1 E. Sinn, *Coord. Chem. Rev., 5,* 313 (1970); G. Kokoszka and R. W. Duerst, *Coord. Chem. Rev., 5,* 209 (1970); B. Jezowska-Trzebiatowska and W. Wojciechowski, *Transition Metal Chem., 6,* 1 (1970); D. Hodgson, *Progr. Inorg. Chem., 19,* 173 (1975).

2 U. Casellato, P. A. Vigato and M. Vidali, *Coord. Chem. Rev., 23,* 31 (1977) and references therein; D. A. Krost and G. L. McPherson, *J. Am. Chem. Soc., 100,* 987 (1978); C. J. O'Connor, D. P. Freyberg and E. Sinn, *Inorg. Chem., 18,* 1077 (1979).

3 A. Dei, D. Gatteschi and E. Piergentili, *Inorg. Chem., 18,* 89 (1979).

4 N. H. Pilkington and R. Robson, *Aust. J. Chem., 23,* 2225 (1970).

5 B. F. Hoskins, N. J. McLeod and H. A. Schaap, *Aust. J. Chem., 29,* 515 (1976).

6 A. Bencini, I. Bertini, D. Gatteschi and A. Scozzafava, *Inorg. Chem., 17,* 3194 (1978).

7 G. F. Kokoszka, H. C. Allen, Jr. and G. Gordon, *J. Chem. Phys., 46,* 3013 (1967).

8 G. F. Kokoszka and G. Gordon, *Transition Metal Chem., 5,* 181 (1969).