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Exchange Interactions in Copper(II)-Nickel(II) and Nickel(II)-Nickel(II) Pairs in Tetra(μ-benzoato-*O*,*O'*)bis(quinoline)dimetal(II) Complexes

Alessandro Bencini, Cristiano Benelli, Dante Gatteschi,* and Claudia Zanchini

Contribution from the Istituto di Chimica Generale e Inorganica, University of Florence, Laboratorio CNR, Florence, Italy. *Received January 14, 1980*

Abstract: Tetra(μ-benzoato-*O*,*O'*)bis(quinoline)dinickel(II) was prepared and found to be isomorphous to the copper(II) and cobalt(II) complexes previously described. The structure is similar to that of the copper acetate dimer, and the magnetic susceptibility data show an antiferromagnetic coupling, $J = -250$ cm^{-1}. By doping the copper(II) derivative with low concentrations of nickel(II), nickel(II)-copper(II) pairs are obtained, which yield ESR spectra at 4.2 K. They can be interpreted by using an effective spin Hamiltonian with $S = {}^1/_2$, yielding $g_1 = 4.51$, $g_2 = 3.44$, $g_3 = 2.24$. A ferromagnetic coupling between the two metal ions is suggested. The implications on the nature of the exchange interactions in the copper acetate type dimers are discussed.

The number of articles which have appeared concerning the electronic structure of copper acetate type dimers is exceedingly large.[1-6] However there is not yet a full general agreement on the nature of the exchange interaction, and direct and superexchange mechanisms are occasionally advocated.[7-12]

Although copper(II) readily forms dimers with many carboxylic acids, the corresponding complexes with other metal ions of the first transition series are not common, if chromium(II) is excepted.[1] Recently the dimeric complex tetra(μ-benzoato-*O*,*O'*)bis(quinoline)dicobalt(II) has been reported and characterized.[13-15] The complex has been shown to be isomorphous to the copper(II) analogue.[16] Its magnetic properties are difficult to interpret, since a quasi-degenerate ground level is expected for a square-pyramidal cobalt(II) complex,[17,18] and the temperature dependence of the magnetic susceptibility of the dimer cannot be rationalized by using only one parameter, J. However, it is apparent that an antiferromagnetic coupling is operative.[13]

The magnetic properties of a nickel(II) dimer, with the copper acetate type structure, should be simpler to handle, since the ground state of a square-pyramidal nickel(II) is orbitally nondegenerate.[17,18] We have now been able to prepare the complex tetra(μ-benzoato-*O*,*O'*)bis(quinoline)dinickel(II), $Ni_2(Bz)_4(Quin)_2$, for which some data were available in the literature,[19] which is isomorphous to the cobalt(II) and copper(II) analogues. We were able to dope the copper complex with some nickel and wish to report here the ESR spectra of the nickel(II)-copper(II) pairs.

Table I. Principal g Values and Directions[a] for Nickel-Doped $Cu_2(Bz)_4(Quin)_2$

g			
4.51 (1)	0.1294	−0.4986	0.7942
3.44 (2)	0.9076	−0.8403	0.4114
2.24 (1)	0.3453	−0.4083	−0.8451

[a] The reference axes correspond to the crystallographic ones *abc*.

Experimental Section

$\mathbf{Ni_2(Bz)_4(Quin)_2}$ was prepared by refluxing for some hours in benzene equimolar amounts of nickel benzoate and quinoline in the presence of benzoic acid and triethyl orthoformate. The metal benzoate and the final product are insoluble in the organic solvent. The dimer is obtained as a microcrystalline powder. If the reaction is made in toluene and the reaction mixture is kept at ~80 °C, also single crystals can be obtained. Because of the insolubility of the complex in the common solvents no recrystallization was possible. Anal. Calcd for $Ni_2C_{46}H_{34}N_2O_8$: C, 64.23; H, 3.98; N, 3.25. Found: C, 63.61; H, 4.06; N, 3.45. The single crystals were also analyzed through Weissenberg techniques and they were found to be isomorphous to the cobalt and copper analogues.

$\mathbf{Cu_2(Bz)_4(Quin)_2}$ was prepared as reported elsewhere.[16] $\mathbf{(Cu,Zn)_2(Bz)_4(Quin)_2}$ and $\mathbf{(Cu,Ni)_2(Bz)_4(Quin)_2}$ were prepared with the method previously described, starting from equimolar mixtures of the metal benzoates.

Single crystal ESR spectra were recorded with the apparatus previously described.[20] Q-band spectra (35 GHz) were recorded with a Varian E-266 cavity equipped with variable-temperature accessory.

Magnetic susceptibility data were obtained with a Faraday balance equipped with a Bruker BMN 50/50 electromagnet and a R-100 Cahn microbalance. The cooling apparatus was a CF 200 flow cryostat of Oxford Instruments Co.

Results

The diffuse reflectance spectra of $Ni_2(Bz)_4(Quin)_2$ are shown in Figure 1. They are similar to those reported for monomeric square-pyramidal nickel(II) complexes, in the same way as the spectra of the corresponding cobalt(II) and copper(II) complexes are similar to the spectra of the parent monomeric compounds.[15] The temperature dependence of the magnetic susceptibility of the nickel complex is shown in Figure 2. It can be analyzed by using the Bleaney-Bowers equation,[21] yielding $J = -250$ cm^{-1}, $g = 2.5$. The isotropic exchange in the spin Hamiltonian has the form $-J\mathbf{S}_1\cdot\mathbf{S}_2$. Although these results may be slightly altered by allowing for paramagnetic impurities[22] and effects associated with the zero

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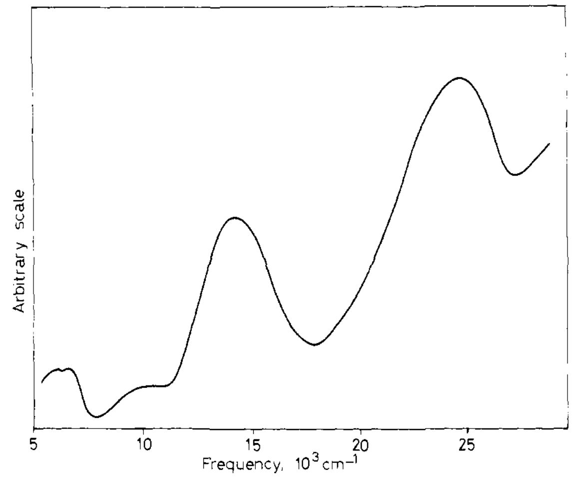

Figure 1. Diffuse reflectance spectrum of $Ni_2(Bz)_4(Quin)_2$.

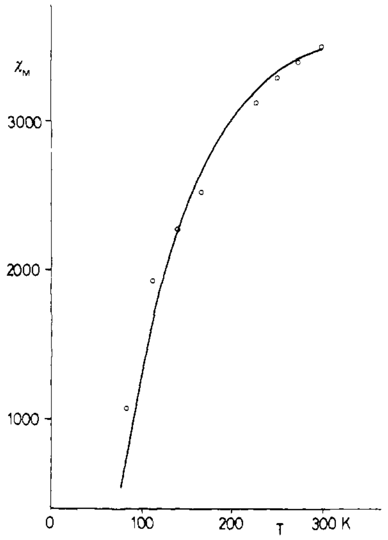

Figure 2. Temperature dependence of magnetic susceptibility of $Ni_2(Bz)_4(Quin)_2$.

field splitting of individual nickel(II) ions, the value of J should be correct within 20 cm^{-1}. Similar results were previously reported.[19] The corresponding curve for $Cu_2(Bz)_4(Quin)_2$ gives $J = -280$ cm^{-1}, using the g values found in the ESR spectra (see below).

The room temperature ESR spectra of nickel(II)-doped $Cu_2(Bz)_4(Quin)_2$ are identical with those of the pure copper complex. The Q-band spectra are shown in Figure 3. The lowest field features correspond to the $\Delta M = 2$ transitions. It must be noted that in this case also the transition relative to crystallites having the magnetic field in the molecular plane is resolved, beyond the more favorable orientation corresponding to H_{min}.[23,24] Using the reported formulas,[25,26] the spin Hamiltonian parameters are evaluated as $g_{\parallel} = 2.35$, $g_{\perp} = 2.06$, $D = 0.36$ cm^{-1}, $E \simeq 0$, $A_{\parallel} = 69 \times 10^{-4}$ cm^{-1}. Single-crystal spectra confirm these values, and show that $g_{\parallel}$ is within error parallel to the Cu–Cu direction. They can be compared to those observed in the zinc-doped $Cu_2(Bz)_4(Quin)_2$ complex, which yields $g_{\parallel} = 2.35$, $g_{\perp} = 2.06$, $A_{\parallel} = 138 \times 10^{-4}$ cm^{-1}.

On cooling the signals due to the copper–copper pairs disappear, until eventually at very low temperatures a new spectrum sets in.

The 9-GHz ESR spectra of the nickel-doped $Cu_2(Bz)_4(Quin)_2$ at 4.2 K are shown in Figure 4. They can be interpreted by using an effective spin Hamiltonian with $S = {}^1/_2$, yielding $g_1 = 4.51$, $g_2 = 3.44$, $g_3 = 2.24$, $A_3 = 94 \times 10^{-4}$ cm^{-1}. Single-crystal spectra confirm that the transitions are within a Kramers doublet. The angular dependence of the g^2 values is given in Figure 5. Although in an orthorhombic crystal it is not possible to assign unambiguously the observed g values to one specific molecule,[27] it seems reasonable to assign the **g** tensor to the molecule with which it makes the smallest angles with the relevant bonding features. The orientation of **g** in the molecule, according to this choice, is shown in Figure 6. The principal g values and directions are given in

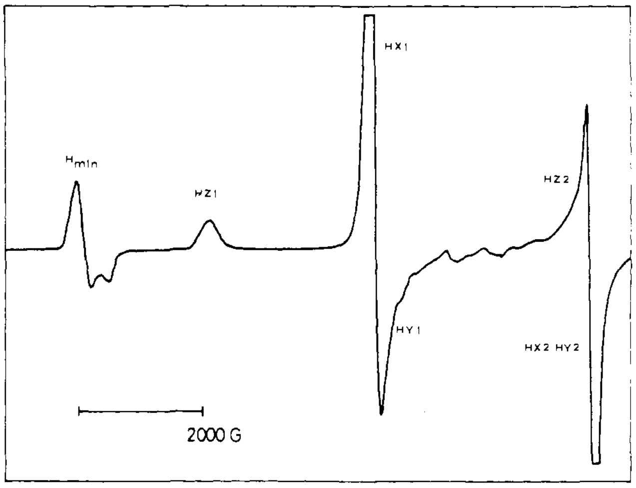

Figure 3. Polycrystalline powder spectra of nickel(II)-doped $Cu_2(Bz)_4(Quin)_2$ recorded at Q-band frequency at 293 K, in the range 4000–14 000 G.

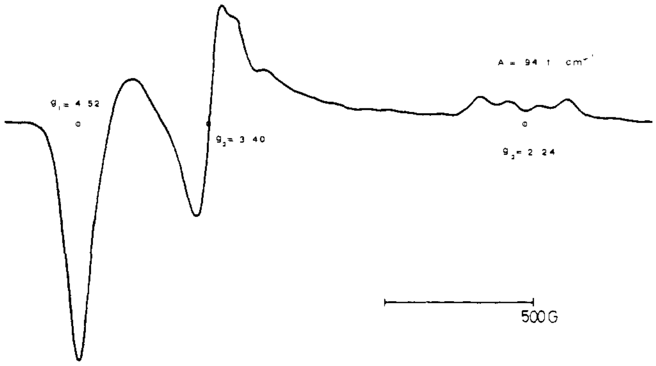

Figure 4. Polycrystalline powder spectra of nickel(II)-doped $Cu_2(Bz)_4(Quin)_2$ recorded at X-band frequency at 4.2 K, in the range 1200–3400 G.

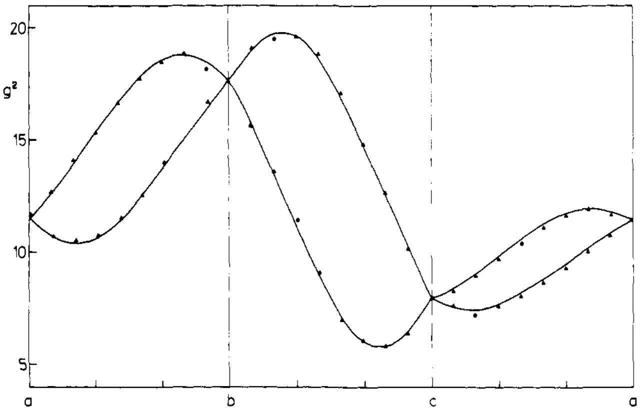

Figure 5. Angular dependence of the g^2 values in the rotations along the crystallographic axes c, a, b. The curves correspond to the least-squares fits to the experimental points.

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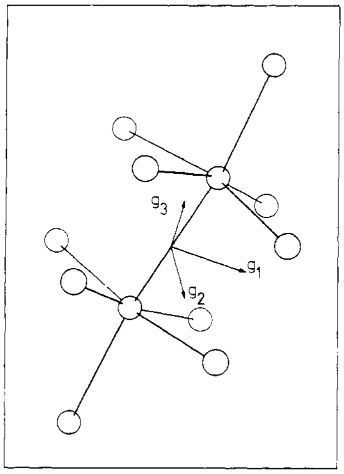

Figure 6. The orientation of the principal axes of **g** within the molecular frame.

Table I. The main feature is that g_3 is making an angle of ~14° with the Cu-Cu direction.

The temperature dependence of the ESR spectra has shown that the intensity of the signal decreases with increasing temperature. Further, the lines broaden dramatically so that above ≃30 K the signal cannot be detected.

Discussion

The ESR spectra of nickel-doped $Cu_2(Bz)_4(Quin)_2$ seen in the range 4.2–30 K are attributed to copper(II)–nickel(II) pairs. The allowed spin states of the couple are $S = {}^1/_2$ and $S = {}^3/_2$. The single-crystal data show unambiguously that the transitions are within a Kramers doublet and the g values suggest that the $\pm{}^1/_2$ components of $S = {}^3/_2$ are most likely responsible for the observed spectra.[28] As a matter of fact the g values might be attributed to a true $S = {}^1/_2$ state only assuming a large orbital contribution which must be ruled out since both copper(II) and nickel(II) have orbitally nondegenerate ground states. In the hypothesis of a large zero-field splitting in the $S = {}^3/_2$ state, the effective g' values are related to the true g values according to[29]

$$g_x' = g_x\left(1 + \frac{1 - 3\lambda}{(1 + 3\lambda^2)^{1/2}}\right)$$
$$g_y' = g_y\left(1 + \frac{1 + 3\lambda}{(1 + 3\lambda^2)^{1/2}}\right) \qquad (1)$$
$$g_z' = g_z\left(1 - \frac{2}{(1 + 3\lambda^2)^{1/2}}\right)$$

where $\lambda = E/D$. The zero-field splitting of the $S = {}^3/_2$ state must be given by[30,31]

$$D = \frac{1}{3}D_{\mathrm{Ni}} + \frac{1}{3}D_e \qquad (2)$$

where D_{Ni} is the zero-field splitting of an individual nickel ion and D_e is the zero-field splitting originated from the exchange and dipolar interaction in the couple. The latter presumably is not very large: it is 0.36 cm^{-1} in the Cu-Cu couple. D_{Ni}, however, is expected[28] to be of the order of 10 cm^{-1}, so that a large zero-field splitting is anticipated also for the $S = {}^3/_2$ states.

Relations 1 cannot be used for obtaining the true g values and λ, since four unknowns are present. However, if g_x is assumed to be equal to g_y,[28] and the observed anisotropy in the g values is attributed to the anisotropy in the zero-field splitting, it is possible to calculate $g_\parallel = 2.30$, $g_\perp = 2.00$, $\lambda = -0.090$. In this analysis perhaps the most meaningful parameter is $g_\parallel$.

The g values in the pairs are related to those of the individual ions according to[30,31]

$$g = \frac{2}{3}g_{\mathrm{Ni}} + \frac{1}{3}g_{\mathrm{Cu}} \qquad (3)$$

so that using the above calculated g values for the pair and the observed g_{Cu} values, obtained from the pure and zinc doped $Cu_2(Bz)_4(Quin)_2$ spectra, one finds $g_{\parallel\mathrm{Ni}} = 2.27$, $g_{\perp\mathrm{Ni}} = 1.99$. The latter value does not seem to be meaningful, while the former compares well with the values expected for tetragonal nickel complexes.[28]

The temperature dependence in the ESR spectra shows that the signal due to the Ni–Cu pairs decreases in intensity on increasing temperature so that the Kramers doublet within which the transition occurs must be the ground level. The fact that no signal attributable to the $S = {}^1/_2$ state is detected in the range 4.2–30 K allows us to estimate that J must be positive and no smaller than 20 cm^{-1}. A strong ferromagnetic coupling in a d^8–d^9 couple in a complex with a similar structure had been previously reported.[32,33] In that case it was a mixed valence compound with formally a nickel(I) and a nickel(II), and J was estimated to be very large, >300 cm^{-1}.

In order to justify the ferromagnetic coupling it is necessary to determine the order of the d orbitals for the individual ions. This is best accomplished through an AO approach.[34] The calculated values can be most easily compared with the spectral properties of the copper complexes.

Although symmetry requirements are not needed in the calculation, for the sake of simplicity it was assumed a C_{4v} symmetry, with a N–Cu–O angle of 96°, corresponding to the average value seen in the X-ray structure.[16] The required bonding parameters are e_σ^{O}, $e_{\pi\parallel}^{\mathrm{O}}$, $e_{\pi\perp}^{\mathrm{O}}$ (∥ and ⊥ refer to the interaction ∥ and ⊥ to the C_{4v} axis, respectively), and e_σ^{N}, e_π^{N}. e_π^{N} was assumed as isotropic, in order to preserve C_{4v} symmetry. The calculated transitions are $x^2 - y^2 \rightarrow z^2$, 6942; $x^2 - y^2 \rightarrow xy$, 11 920; $x^2 - y^2 \rightarrow xz, yz$, 13 300 cm^{-1}, using $e_\sigma^{\mathrm{O}} = 4600$, $e_{\pi\parallel}^{\mathrm{O}} = 0$, $e_{\pi\perp}^{\mathrm{O}} = 350$, $e_\sigma^{\mathrm{N}} = 2200$, $e_\pi^{\mathrm{N}} = 50$ cm^{-1}. These values compare well with the electronic spectra of $Cu_2(Bz)_4(Quin)_2$, where a broad band with a maximum at ~13 700 cm^{-1} and a shoulder at ~7000 cm^{-1} are observed. Also the order of the levels corresponds to that previously suggested for similar complexes.[35,36] With the same calculation also the g and A values were obtained, by setting $\zeta = 830$ cm^{-1}, $k = 0.830$, $\kappa = 0.407$, $P = 0.0237$ cm^{-1}. k is the Stevens orbital reduction factor,[37] $P\kappa$ is the isotropic hyperfine term, $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$.[38] The calculated values are $g_\parallel = 2.36$, $g_\perp = 2.06$, $A_\parallel = 132 \times 10^{-4}$ cm^{-1}, $A_\perp = 12 \times 10^{-4}$ cm^{-1}, in excellent agreement with the experimental values of the Cu–Zn couple.

Assuming that the order of the levels remains unaltered on passing from copper to nickel, the experimental J value in the Ni–Cu couple can be justified, decomposing the exchange mechanism according to the relation[39,40]

$$J = \tfrac{1}{2}(J_{x^2-y^2,x^2-y^2} + J_{x^2-y^2,z^2}) \qquad (4)$$

where $J_{i,j}$ represents the exchange integral between the indicated d orbitals. $J_{x^2-y^2,x^2-y^2}$ must be antiferromagnetic, as shown by the data relative to $Cu_2(Bz)_4(Quin)_2$, while $J_{x^2-y^2,z^2}$ must be ferromagnetic, since the $x^2 - y^2$ orbital on copper and z^2 on nickel are orthogonal and in mutual contact.[41,42] The experimental data

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require that this is indeed the dominant contribution. In using (4) it was assumed that the ground state is given by the configuration ($x^2 - y^2$, z^2). This is a good assumption since in C_{4v} symmetry no excited levels of the same symmetry can mix into the ground level.[17]

These data, together with the magnetic susceptibility data of $Ni_2(Bz)_4(Quin)_2$, allow us to gain a deeper insight into the mechanism of exchange in copper acetate type dimers. The obtained J value is quite close to that of $Cu_2(Bz)_4(Quin)_2$, while the coupling constants in Ni–Ni pairs are generally found to be much smaller than those in the corresponding Cu–Cu pairs.[43] In the nickel dimer the experimental J is expected to be given by[39,40]

$$J = \tfrac{1}{4}(J_{x^2-y^2,x^2-y^2} + J_{x^2-y^2,z^2} + J_{z^2,x^2-y^2} + J_{z^2,z^2}) \qquad (5)$$

If we set $J_{x^2-y^2,z^2} = 0$, we are actually underestimating this contribution as shown by the previous arguments. This gives a lower limit to the sum $J_{x^2-y^2,x^2-y^2} + J_{z^2,z^2} = 1000\ \text{cm}^{-1}$. Since $J_{x^2-y^2,x^2-y^2}$ is 300 cm^{-1} for the copper dimer, and assuming that it is not greatly changed on going to the nickel pair, it must be concluded that $J_{z^2z^2}$ is providing the largest contribution to the antiferromagnetic coupling in $Ni_2(Bz)_4(Quin)_2$. This conclusion is in agreement with a direct mechanism according to which the z^2 orbitals are metal–metal σ bonding, while the $x^2 - y^2$ orbitals are δ bonding. For a superexchange mechanism the $x^2 - y^2$ orbitals are σ antibonding relative to the in-plane ligands, and any realistic pathway must start from this consideration. The z^2 orbitals are also σ antibonding, but they are expected to be far less so, as compared to the $x^2 - y^2$ orbitals. Therefore in order to justify a larger antiferromagnetic J_{z^2,z^2} interaction as compared to $J_{x^2-y^2,x^2-y^2}$ it must be assumed a sizable direct contribution to the exchange mechanism. On the other hand, it cannot be the only mechanism since in this case $J_{x^2-y^2,x^2-y^2}$ should be expected to be at least one order of magnitude smaller than J_{z^2,z^2}.

Also a π superexchange mechanism has been popular in the interpretation of the magnetic data of copper acetate type dimers.[11,12] Since the $x^2 - y^2$ orbitals are not π antibonding, the interaction with xy orbitals, allowed by spin–orbit coupling, must be advocated. While this cannot be excluded in the present case, it must be mentioned that J values quite close to that of copper acetate have been found in copper oxalate dimers,[44] where a σ pathway has been demonstrated.[45]

The observed copper(II) hyperfine splitting deserves some comments. In the dinuclear unit the copper nucleus is under the influence of the unpaired electrons localized on both the copper and nickel nuclei. The relevant spin Hamiltonian terms can be written as[46]

$$H = \mathbf{S}_1 \cdot \mathbf{A}_1 \cdot \mathbf{I}_{Cu} + \mathbf{S}_2 \cdot \mathbf{A}_2 \cdot \mathbf{I}_{Cu}$$

where $\mathbf{S}_1$ and $\mathbf{S}_2$ are the spins of copper and nickel, respectively, and $\mathbf{A}_1$ and $\mathbf{A}_2$ are the relevant hyperfine coupling tensors. Using vector coupling techniques, it is possible to show that the hyperfine splittings in the $S = {}^1/_2$ and $S = {}^3/_2$ states of the dinuclear complex are[30,31]

$$A_{3/2} = \tfrac{1}{3}A_1 + \tfrac{2}{3}A_2 \qquad (6)$$

$$A_{1/2} = -\tfrac{1}{3}A_1 + \tfrac{4}{3}A_2$$

In this notation A_1 would be the hyperfine coupling constant of the mononuclear copper complex, which can be estimated from the data of the Cu–Zn pair, and A_2 is the transferred hyperfine coupling constant (STHI).[47]

Evidence for the operation of the transferred hyperfine constant has been found in some copper–nickel complexes, where the value of A observed in the pair is $\simeq$15% smaller than ${}^1/_3 A_{Cu}$.[47]

No such evidence was found for copper acetate type dimers[48] and also in the present case the observed A value in the Cu–Cu pair is very close to half the value found in the Cu–Zn pair. In the Cu–Ni pair, however, the observed A is distinctly larger than the value of 46 × 10^{-4} cm^{-1} which would be expected from the values of 139 × 10^{-4} cm^{-1} observed in the Cu–Zn couple. As compared to the previously reported cases, where the hyperfine coupling relative to the $S = {}^1/_2$ state was resolved, a change in the sign in the STHI must be expected, using relation 6. The magnitude of the effect is, however, surprising, and the only rationale we are able to offer is that the nickel ion is strongly interacting via the z^2 orbital with the copper nucleus. If this hypothesis is true, the copper hyperfine coupling constant in copper–nickel couples should be very sensitive to metal–metal distances.

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