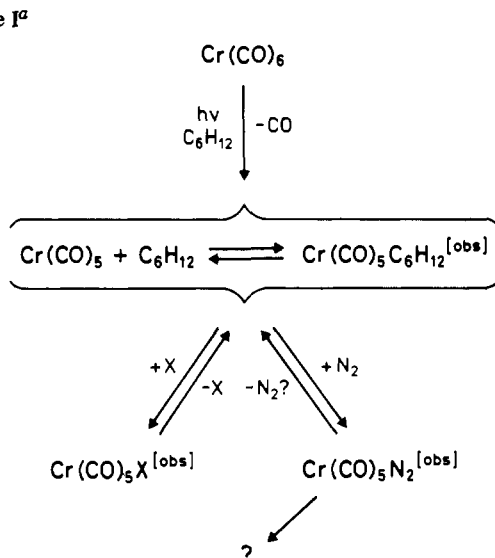


Scheme 1^a

^a [obs] = transient observed; X = unknown trace impurity. Note that reaction with N_2 is much more important than with X under our conditions.

the technique of flash photolysis with infrared detection has become. Notably in the case of $Cr(CO)_5N_2$, a detailed infrared study in room-temperature solution (q.v.) can now be directly compared with low-temperature work^{3,5} (see Table I). The opportunity for such a comparison is rarely possible. There is clearly a scope for a wide range of applications of solution flash photolysis with infrared detection.¹⁷

The unique use of the specifically monolabeled compound $Cr(CO)_5(^{13}CO)$, the synthesis of which has recently been accomplished in our laboratory,¹² proved valuable in the interpretation of the infrared spectrum of $Cr(CO)_5N_2$. More extensive ^{13}CO isotopic studies of $Cr(CO)_5$ species using this compound should now also be possible.

Acknowledgment. We thank Dr. M. Poliakoff for valuable discussions, V. Skibbe for preparing the sample of $Cr(CO)_5(^{13}CO)$, and K. Sandmann for able technical assistance.

Registry No. $Cr(CO)_6$, 13007-92-6; $Cr(CO)_5N_2$, 34416-63-2; $Cr(CO)_4(^{13}CO)N_2$, 92126-01-7; C_6H_{12} , 110-82-7; N_2 , 7727-37-9.

(17) Other obvious and important targets of flash photolysis with infrared detection are thermally equilibrated excited states. The short lifetimes and, in the case of other than metal carbonyl compounds, considerably weaker absorptions demand improvements in sensitivity and time resolution such as are in preparation, including pulsed laser excitation and laser diode infrared sources. An interesting alternative to our approach, albeit restricted as yet to the long nanosecond to microsecond time scale, has recently been presented. The pulsed continuum infrared radiation of a laser-produced plasma is used as an extraordinarily powerful source (Adamson, A. W.; Cimolino, M. C. *J. Phys. Chem.* **1984**, *88*, 488). We thank Professor Adamson for the communication prior to publication.

Contribution from the Laboratoire de Spectrochimie des Eléments de Transition, ERA No. 672, Université de Paris-Sud, 91405 Orsay, France

Hyperfine Parameters in an Exchange-Coupled Copper(II)-Nickel(II) Pair. Relation to the Local Hyperfine Splitting

S. R. Desjardins,¹ I. Morgenstern-Badarau,* and O. Kahn*

Received November 3, 1983

Heterobimetallic systems are particularly interesting in the theory of exchange interactions. They provide the possibility

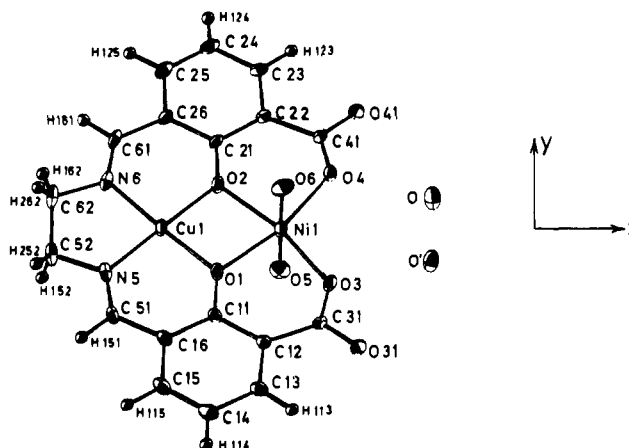


Figure 1. Perspective view of $[CuNi]$, with the x and y molecular axes (from ref 8).

of comparing spin-Hamiltonian parameters for each pair state with the local parameters associated with the single-ion ground states.^{2-7,11}

To obtain all the expected information, it is necessary to have at one's disposal the pure material for the magnetic susceptibility study and a host material doped with the coupled system for the observation of hyperfine structure in the EPR spectrum. To our knowledge, till now, these two conditions were not fulfilled for any heterobimetallic system. The host lattice must present two characteristics: to be isostructural with the pure material and to be EPR silent in the temperature range where the spectra are recorded. We had previously investigated the complex $CuNi(fsa)_2en(H_2O)_2 \cdot H_2O$, noted $[CuNi]$, where $(fsa)_2en^{4-}$ is the bichelating ligand derived from the Schiff base 1,2-bis[(2-hydroxy-3-carboxybenzylidene)-amino]ethane.⁸ Magnetic and EPR properties were compared to those of the isostructural $[CuMg]$ and $[NiNi]$ complexes, in which only one of the two metal ions is paramagnetic. We determined the energy gap $-3J/2 = 213 \text{ cm}^{-1}$ between the doublet and quartet states arising from the antiferromagnetic coupling. We found quite a satisfying agreement between the observed g values of the ground doublet state of $[CuNi]$ and those calculated from the g values of the noncoupled $[CuMg]$ and $[NiNi]$ compounds.

Since we worked with pure materials, we were not able to carry out the same investigation for the hyperfine tensors. However, $[CuNi]$ is potentially a good candidate for checking the validity of similar relations between pair and local hyperfine parameters. Such an investigation became possible when we realized that $[CuCo]$ was an ideal host lattice for this purpose. $[CuCo]$,⁹ $[CuNi]$, and $[CuMg]$,¹⁰ have identical trigonal structures with three molecules per unit cell. The structure of one of these compounds, namely $[CuNi]$, is recalled in Figure 1, with the in-plane x and y molecular axes. The z molecular axis is collinear with the c trigonal axis.

- (1) Present address: GTE Laboratories, Waltham, MA 02254.
- (2) Kokoszka, G. F.; Allen, H. C., Jr.; Gordon, G. *J. Chem. Phys.* **1967**, *46*, 3020.
- (3) Chao, C. C. *J. Magn. Reson.* **1973**, *10*, 1.
- (4) Paulson, J. A.; Krost, D. A.; McPherson, G. L.; Rogers, R. D.; Atwood, J. L. *Inorg. Chem.* **1980**, *19*, 2519.
- (5) Buluggiu, E. *J. Phys. Chem. Solids* **1980**, *41*, 1175; **1982**, *43*, 997.
- (6) Banci, L.; Bencini, A.; Benelli, C.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1981**, *20*, 1399.
- (7) Banci, L.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1981**, *20*, 2734.
- (8) Morgenstern-Badarau, I.; Rerat, M.; Kahn, O.; Jaud, J.; Galy, J. *Inorg. Chem.* **1982**, *21*, 3050.
- (9) Mikuriya, M.; Okawa, H.; Kida, S.; Ueda, I. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2920.
- (10) Beale, J. P.; Cunningham, J. A.; Phillips, D. J. *Inorg. Chim. Acta* **1979**, *33*, 113.
- (11) Banci, L.; Bencini, A.; Dei, A.; Gatteschi, D. *Inorg. Chem.* **1981**, *20*, 393.

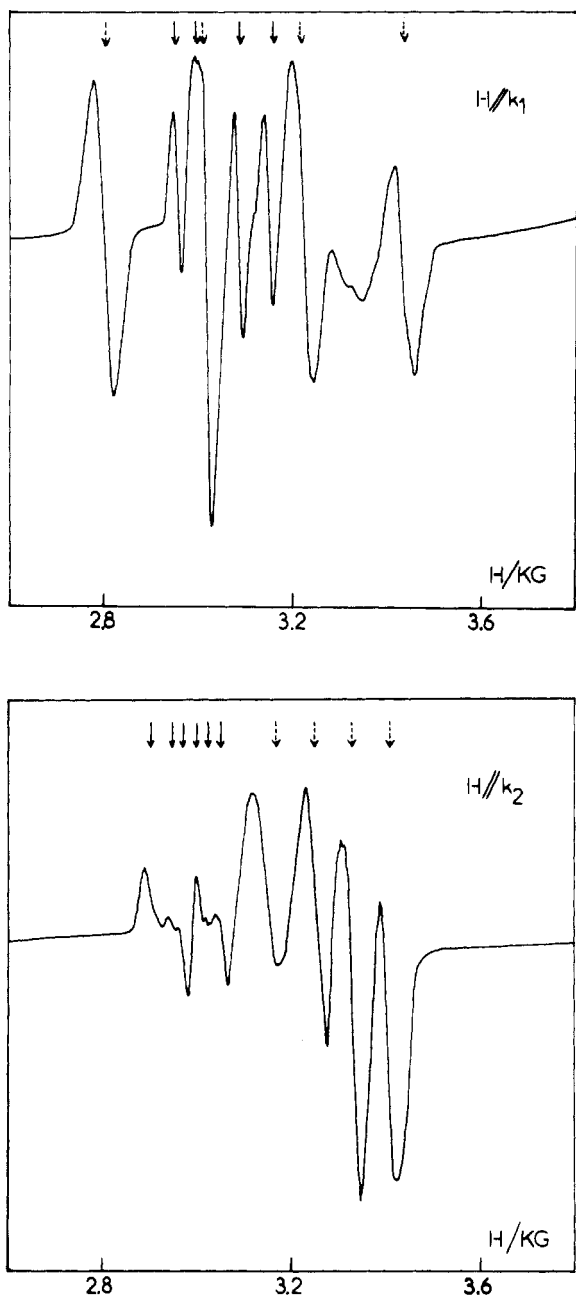


Figure 2. EPR spectra along the k_1 and k_2 directions. The peaks associated with [CuMg] are indicated by dashed arrows and those associated with [CuNi] by full arrows.

Cu(II) occupies the inside site with a strict planar surrounding; the other metal ion occupies the outside site with a pseudo-octahedral coordination. The molecular symmetry is very close to C_{2v} . In [CuCo], the heterobimetallic units pile up clockwise along the unique axis of the trigonal lattice (space group $P3_2$). In [CuNi] and [CuMg], they pile up counterclockwise (space group $P3_1$).⁸ [CuCo] is EPR transparent at any temperature in the range 4.2–300 K.

Experimental Section

All the data presented here were first obtained on unintentionally Mg- and Ni-doped crystals of $\text{CuCo}(\text{fsa})_2\text{en}(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ prepared as previously described.⁹ A first hint of the presence of EPR-active heterobinuclear impurities was obtained through the observation of a rather complex powder EPR spectrum at 4.2 K. A complete single-crystal study was then performed by using a Bruker ER 200 D spectrometer equipped with an Oxford Instruments continuous-flow cryostat, a Hall probe, and a Hewlett-Packard frequency meter. The single crystal, a rhombohedron, was mounted on a Perspex rod and rotated around the three orthogonal axes k_1 , k_2 , and k_3 (see Figure

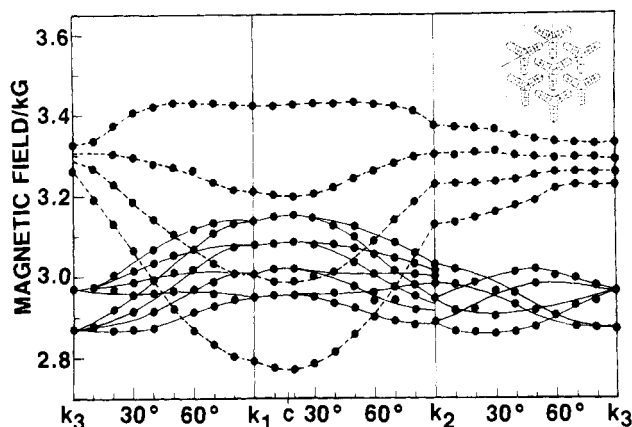


Figure 3. Angular dependence of the X-band EPR spectra in three orthogonal planes for [CuCo] doped with Ni and Mg, at 10 K. The full and dashed curves are visual aids connecting the [CuNi] and [CuMg] experimental points, respectively. k_3 lies in the ab plane and is parallel to a y molecular axis (as defined in ref 8); k_1 lies 17° from c and 73° from the ab plane; k_2 lies 73° from c and 163° from the ab plane. A schematic representation of the crystal packing perpendicular to the c axis is recalled in the upper right corner.

Table I. g and A Tensor Components for [CuMg] and [CuNi]^a

	g tensor	A tensor
[CuMg]	$g_{\parallel} = 2.18$ (1) $g_{\perp} = 2.06$ (1)	$A_{\parallel} = 222$ (1) $\times 10^{-4}$ cm^{-1} $A_{\perp} = 29$ (1) $\times 10^{-4}$ cm^{-1}
[CuNi]	$g_{\parallel} = 2.22$ (1) $g_x = 2.25$ (2) $g_y = 2.36$ (2)	$A_{\parallel} = 69$ (1) $\times 10^{-4}$ cm^{-1} $A_{\perp} \leq 10 \times 10^{-4}$ cm^{-1}

^a Estimated standard deviations in the last significant figure are given in parentheses.

3) in steps of 10° , by means of a goniometer. k_3 was perpendicular to the c trigonal axis and to one of the rhombohedral edges. Since there is strong evidence that the projections of the rhombohedral edges in the ab plane are parallel to the copper-metal axes (x molecular axes), it can be inferred that k_3 is parallel to a y molecular axis.

Two groups of lines were observed whose angular variation and corresponding values of the g tensor could be assigned as belonging to [CuNi] and [CuM_d] (where M_d is a diamagnetic ion), respectively. This assignment was confirmed by repeating the same experiment on intentionally doped crystals obtained by evaporation of a methanolic solution containing $\text{CuCo}(\text{fsa})_2\text{en}(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ and $\text{CuNi}(\text{fsa})_2\text{en}(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$ in a 9:1 ratio. The shape of the features attributed to [CuNi] was then unchanged but their intensity was largely amplified. Finally, chemical analysis of the unintentionally doped crystals revealed Ni:Co and Mg:Co ratios of 5×10^{-4} and 10^{-3} , respectively. As examples, the two spectra along the k_1 and k_2 axes are shown in Figure 2.

Results and Discussion

All spectra were recorded around 10 K. It can be noticed here that the magnetic behavior of both pure [CuNi] and [CuMg] complexes in the low-temperature range revealed intermolecular interactions.⁸ In the present case, this effect should be negligible since the proportion of EPR-active pairs is of the order of 10^{-3} . Let us examine now each of the two pairs.

[CuMg]. The interpretation of the EPR spectra is straightforward. Four equidistant lines (Figure 3, dashed lines) are recorded for every direction of the magnetic field. They are attributed to the hyperfine interaction of the unpaired electron with the copper nucleus, $I = 3/2$. The g and A parameters deduced from the angular dependence of the g^2 and A^2g^2 tensors are given in Table I. Within experimental uncertainties, both g and A are found to be axial, with their maximum principal values along the c axis. This axiality explains why the three binuclear sites of the unit cell appear magnetically equivalent in this case. The agreement between

the g tensor components reported here and those of the pure [CuMg] complex⁸ is found to be good, particularly in view of the uncertainty of the measurement of g_{\parallel} in the powder spectrum of the pure material.

[CuNi]. The [CuNi] spectra (Figure 3, full lines) are much more difficult to analyze than those of [CuMg], since the resonant fields of the three magnetically inequivalent binuclear sites are distinct. Again, hyperfine structure is present, splitting each resonance of the k_3k_1 and k_1k_2 planes into four equidistant lines. Because of the very low abundance (1.19%) of the ⁶¹Ni isotope with $I = 3/2$, this hyperfine structure arises exclusively from the coupling of the $S = 1/2$ electronic ground state with the $I = 3/2$ nuclear spin of copper. The contributions of the three magnetically inequivalent sites are clearly displayed in the k_2k_3 plane, whose normal was found to be only 17° from the trigonal axis. A total of twelve lines were expected in this plane, but only three broad envelopes are resolved, in agreement with the very weak value of A_{\perp} (see below). The three envelopes are out of phase by 60° and two of them intersect every 30° . When H is parallel to k_3 , the intensity of the high-field line is about twice that of the low-field line; two of the three magnetic sites, with their molecular x axes 30° from H , contribute to the high-field line, while only one magnetic site, with its molecular y axis parallel to H , corresponds to the low-field line. Inversely, when H is parallel to k_2 , the low-field group of lines, which now represents the contributions of the two magnetic sites with their molecular y axes approximately 30° from H , becomes more intense than the high-field group. In the k_3k_1 and k_2k_1 planes, where H is rotated from the k_3 or the k_2 axis toward the c axis, eight hyperfine lines collapse into four equally intense lines, as expected.

The g and A parameters deduced from the analysis of the angular dependence of the g^2 and g^2A^2 tensors for each of the three magnetic sites are given in Table I. The minimum principal g value is found along the c axis; its value is 2.22, in excellent agreement with that determined from the study of the pure compound.⁸ In contrast, whereas the g tensor of the pure compound appears to be axial, in the diluted compound it exhibits a rhombic symmetry with $g_x = 2.25$ and $g_y = 2.36$, where the principal magnetic axes coincide with the molecular axes x and y . The maximum principal A value, equal to $69 \times 10^{-4} \text{ cm}^{-1}$ is found along the c axis. In the ab plane, the hyperfine parameter is found smaller than $10 \times 10^{-4} \text{ cm}^{-1}$ and cannot be determined with accuracy.

The appropriate spin Hamiltonian to describe the low-lying states in [CuNi] is

$$\mathcal{H} = \beta H \cdot (g_{\text{Cu}} \hat{S}_{\text{Cu}} + g_{\text{Ni}} \hat{S}_{\text{Ni}}) + \hat{S}_{\text{Ni}} \cdot \mathbf{D} \cdot \hat{S}_{\text{Ni}} - J \hat{S}_{\text{Cu}} \cdot \hat{S}_{\text{Ni}} + \hat{S}_{\text{Cu}} \cdot \mathbf{D}_{\text{CuNi}} \cdot \hat{S}_{\text{Ni}} + \hat{I}_{\text{Cu}} \cdot \mathbf{A}_{\text{Cu}} \cdot \hat{S}_{\text{Cu}} \quad (1)$$

where the meaning of the symbols, but the last one, has already been specified.⁸ The last term is the copper(II) single-ion hyperfine structure term. The spin Hamiltonian associated with the $S = 1/2$ ground pair state is

$$\mathcal{H}_{1/2} = \beta H \cdot g_{1/2} \hat{S} + \hat{I}_{\text{Cu}} \cdot (\mathbf{A}_{\text{Cu}})_{1/2} \hat{S} \quad (2)$$

where the meaning of the symbols is obvious. The relations between $g_{1/2}$, g_{Cu} , and g_{Ni} , on the one hand, $(\mathbf{A}_{\text{Cu}})_{1/2}$ and \mathbf{A}_{Cu} , on the other hand, are

$$g_{1/2} = \frac{4g_{\text{Ni}} - g_{\text{Cu}}}{3} \quad (3)$$

$$(\mathbf{A}_{\text{Cu}})_{1/2} = -\frac{1}{3} \mathbf{A}_{\text{Cu}} \quad (4)$$

We already discussed the validity of relation 3.⁸ As far as the hyperfine interaction is concerned, the validity of relation 4 is nicely checked for the well-determined principal value of the A tensor, since $(A_{\parallel\text{Cu}})_{1/2} = 69 \times 10^{-4} \text{ cm}^{-1}$ and the corresponding value in the same direction for [CuMg] is $A_{\text{Cu}} = 222 \times 10^{-4} \text{ cm}^{-1}$. We find the agreement to be quite good¹²

and definitely better than that found in two similar single-crystal studies.^{2,11} The fact that the smallest value of the hyperfine coupling could not be established is also a check of relation 4 since the perpendicular value for the pair estimated from the corresponding one in [CuMg] should be less than $10 \times 10^{-4} \text{ cm}^{-1}$.

The agreement found between the observed hyperfine parameters in [CuNi] and [CuMg] and those deduced from the spin Hamiltonian (1) suggests that the approximations on which it is based are valid.⁸ These approximations are as follows: (i) the wave functions of the real electrostatic Hamiltonian (including spin-orbit coupling and Zeeman terms) appropriate to describe the low-lying pair states are Heitler-London functions constructed from eigenfunctions of local Hamiltonians; (ii) the coupling between ground configuration ($\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}$) and metal-metal charge-transfer configuration ($\text{Cu}^{\text{III}}\text{Ni}^{\text{I}}$ or $\text{Cu}^{\text{I}}\text{Ni}^{\text{III}}$) is not taken into account. Furthermore, we can specify the range of validity of the relations (3) and (4). In [CuNi], the isotropic exchange is found to be of medium magnitude. But if $|J|$ were very small, the total spin S would not be a good quantum number any longer and the meaning of the Hamiltonian (2) would vanish. At the other extremity, if J were very negative, the Heitler-London description of the low-lying states, which is implicitly required by the spin Hamiltonian (1), would not be appropriate any longer.

Since we did not observe any EPR transition within the upper quartet state of [CuNi], we were not able to check relations relative to zero-field splitting effects, similar to (3) and (4), as has been done with other heterobinuclear systems.^{4,5,7} In order to specify the range of validity of the approximations required by the spin-Hamiltonian formalisms (1) and (2), we shall study other Cu(II)-Ni(II) pairs with smaller doublet-quartet energy gaps. To conclude, we want to emphasize that the [CuNi] complex considered in this note is apparently the first heteropair for which we have both the energy gap between low-lying spin states owing to accurate magnetic measurements on the pure material and the details of the electronic structure of the ground state owing to this EPR study on a doped diamagnetic host lattice. We also wish to point out that [CuCo] could be used as EPR-silent host lattice for investigating the properties of low-lying states in other pairs.¹³

Acknowledgment. S.R.D. thanks the CNRS for a post-doctoral appointment in 1981-1982.

Registry No. CuCo(fsa)₂en(H₂O)₂, 62109-46-0; Mg, 7439-95-4; Ni, 7440-02-0.

(12) One of the reviewers suggested that an additional term in the Hamiltonian (1) of the form $\hat{I}_{\text{Cu}} \cdot \mathbf{A}'_{\text{Cu}} \cdot \hat{S}_{\text{Ni}}$ could account for the weak deviation with regard to relation 4.

(13) In fact, making use of this conclusion, we also prepared [CuCo] doped with Mn with an initial Mn:Co ratio of 1:20. Unfortunately, the EPR spectrum of the resulting well-shaped crystals proved to be of prohibiting complexity.

Contribution from the Department of Chemistry, College of Arts and Sciences, The University of Tokyo, Komaba, Meguro-ku, Tokyo 153, Japan, and ASAI Germanium Research Institute, Izumihoncho, Komae-shi, Tokyo 201, Japan

Germanium-73 Chemical Shifts and Spin-Lattice Relaxation Times of Some Tetrasubstituted Germanes

Yoshito Takeuchi,^{*,†} Toshie Harazono,[†] and Norihiro Kakimoto[†]

Received January 9, 1984

As compared with NMR spectroscopy of other group 4B elements, that of ⁷³Ge has attracted less attention chiefly