

distances and angles were used in our calculations: N-N-(Co₂(CO)₆(μ-N₂) and Ni₂Ph₂(μ-N₂)⁴⁻), 1.35 Å; Co-C, 1.8 Å; C-O, 1.16 Å; Co-Co, 2.46 Å; Co-N, 2.0 Å; P-P, 2.019 Å; Co-P, 2.264 Å; S-S, 2.007 Å; Co-S, 2.228 Å; C-C, 1.335 Å; Co-C, 1.996 Å; N-N(Co₂(CO)₆(μ-N₂H₂)²⁺), 1.37 Å; Co-N,

1.878 Å; CO-Co-CO, 90°; Co-C-O, 180°; C-C-H, 145°; N-N-H, 123°.

Parameters for H, C, N, and O are the standard ones.¹⁵ The parameters for P, S, Co, and Ni are from our previous work^{11,14} and are compiled in Table II.

Registry No. Co₂(CO)₆(μ-N₂), 82838-96-8; Co₂(CO)₆(μ-P₂), 51244-37-2; Co₂(CO)₆(μ-S₂)²⁺, 82838-97-9; Co₂(CO)₆(μ-C₂H₂), 12264-05-0; Co₂(CO)₆(μ-N₂H₂)²⁺, 82838-98-0; Ni₂Ph₂(μ-N₂)⁴⁻, 82838-99-1.

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Exchange Interactions in Heterodinuclear Complexes with One Ion Possessing an Orbitally Degenerate Ground State. Nickel(II)-Cobalt(II) Pairs in Diaquo(1,4-dihydrazinophthalazine)nickel(II) Chloride Hydrate

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The EPR spectra of copper(II)- and cobalt(II)-doped diaquo(1,4-dihydrazinophthalazine)nickel(II) chloride hydrate, Ni₂(dhph)₂(H₂O)₄Cl₄·2H₂O, have been recorded at liquid-helium temperature. Signals attributable to Ni-Co and Ni-Cu pairs were found and assigned on the basis of the hyperfine splitting patterns. In both cases the spectra could be interpreted within a $S = 1/2$ spin Hamiltonian yielding the following: Ni-Cu, $g_1 = 2.07$, $g_2 = 2.21$, $g_3 = 2.25$; Ni-Co, $g_1 = 0.60$, $g_2 = 0.93$, $g_3 = 2.09$. The temperature dependence of the signal intensity of the Ni-Cu pairs shows that the coupling between the two metal ions is antiferromagnetic, as expected for two octahedra sharing an edge. For the Ni-Co pairs, in which the cobalt ion has an orbitally degenerate ground level, a simple model was used to calculate the exchange coupling constants of the nickel ³A_{2g} ground level with the three orbital components of cobalt ⁴T_{1g}. The calculated parameters correspond in any case to antiferromagnetic interactions, the three exchange pathways being essentially identical with each other.

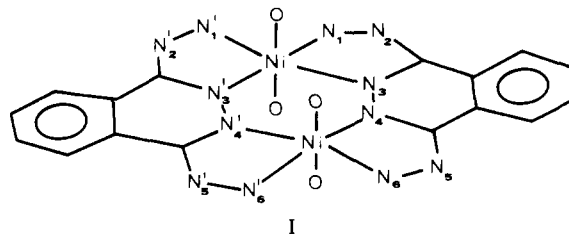
Introduction

Exchange interactions in homo- and heterodinuclear transition-metal complexes are currently much studied,¹⁻⁵ and several theoretical models have been used with some success to correlate the observed coupling constants with the electronic structure of the individual ions.⁶⁻⁸ The main limitation in the theoretical background is that only orbitally nondegenerate ground states can be easily handled. Introducing ground-state orbital degeneracy complicates enormously the patterns of interactions between the two metal ions, and the energy levels of the pairs can be expressed only by using a large number of parameters.⁹ Some cases exist where the treatment has been performed by using models of different sophistication,¹⁰⁻¹³ but as yet no definite trend starts to be apparent for the ex-

change interaction between orbitally degenerate ground states.

A simpler case, which in principle can be handled in a more tractable manner, is that relative to the interaction of an orbitally nondegenerate ion with an orbitally degenerate one.^{14,15} In this case some simple models have been suggested, which have been applied to few experimental cases. In order to check their validity, however, it is necessary to study many more experimental data, trying to correlate the values of the parameters to the electronic structures of the complexes.

Cobalt(II) in an octahedral ligand field has a ground ⁴T_{1g} level. Several dinuclear complexes have been reported in which octahedral cobalt(II) ions are present. An interesting series, for which crystal structure determinations are available, is that of diaquo(1,4-dihydrazinophthalazine)metal(II) chloride hydrate, M₂(dhph)₂(H₂O)₄Cl₄·2H₂O, where metal can be either cobalt or nickel.¹⁶⁻¹⁸ Structure I shows the complex with



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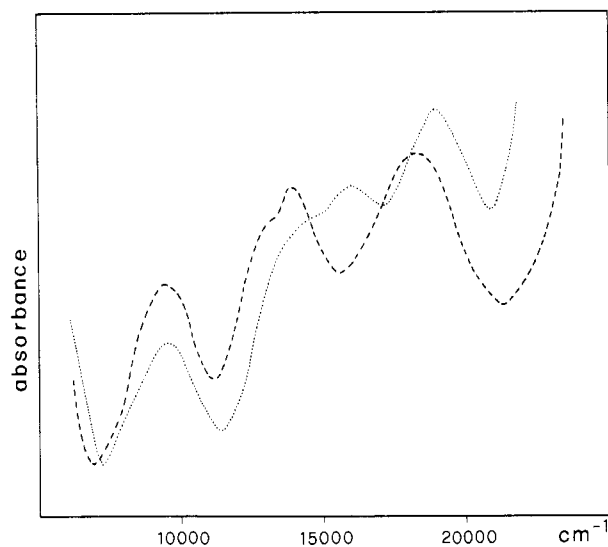


Figure 1. Single-crystal electronic spectra of $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, recorded with the radiation perpendicular to the (001) face: (---) with the electric vector parallel to r ; (···) with the electric vector parallel to s (see text).

nickel. For both of them an antiferromagnetic coupling was observed. By doping the nickel complex with cobalt, we obtained a measurable amount of Ni-Co pairs, which we characterized through EPR spectroscopy. We wish to report here the results of an analysis using a simple model previously described.¹⁴

Experimental Section

The preparation of the $\text{M}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ complexes ($\text{M} = \text{Ni}, \text{Co}$) has been described elsewhere.^{18,19} If in the reaction mixture a little amount of chloride of the M' metal is added to the stoichiometric amount of the metal M chloride, some pairs $\text{M}-\text{M}'$ are obtained in the $\text{M}-\text{M}$ lattice. Single crystals suitable for polarized electronic spectra and EPR spectra were obtained from slow evaporation of aqueous solutions.

The crystals of $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ were found to conform to the reported structure¹⁷ when they were oriented on a Perspex rod with the aid of a polarizing microscope and placed in a Philips PW1100 diffractometer.

Single-crystal EPR spectra were recorded with a Varian E-9 spectrometer operating at X-band frequency (9 GHz). Liquid-helium temperatures were obtained with an Oxford Instruments ESR 9 continuous-flow cryostat.

Single-crystal polarized electronic spectra were recorded with a Cary 14 spectrophotometer using Nicol prisms as polarizers.

Results

Single-Crystal Polarized Electronic Spectra of $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. The reflectance spectra of $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ were previously reported.¹⁷ They were assigned in D_{4h} symmetry. Since the crystals appeared to be dichroic, we recorded also single-crystal spectra. The spectra relative to the (001) face are shown in Figure 1. The two spectra were recorded with the electric vector of the incident radiation parallel to the two extinction directions in this face. Direction r makes an angle of -50° with the positive direction of b , and s is orthogonal to it.

In the range 9000–20 000 cm^{-1} four maxima are detected in the spectrum recorded with the electric vector parallel to s at 9500, 14 000 (sh), 15 900, and 18 900 cm^{-1} . The spectrum parallel to r shows again a peak at 9400 cm^{-1} , of higher intensity compared to that in the s spectrum, a shoulder at 13 000 cm^{-1} and a peak at 13 800 cm^{-1} , and a fourth maximum at 18 200 cm^{-1} .

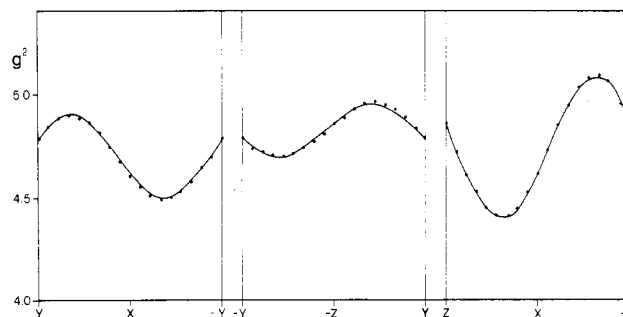


Figure 2. Angular dependence of the g^2 values of the Ni-Cu pair in the three experimental rotations (along the axes defined in Table I). The curves correspond to the least-squares fit of the experimental points.

Table I. Principal g Values and Direction Cosines of the Principal Directions in the Laboratory Frame^a for Ni-Cu and Ni-Co Pairs

Ni-Cu		
$g^b = 2.07 (1)$	$g = 2.21 (1)$	$g = 2.25 (1)$
-0.7514	0.3394	-0.5659
0.4126	0.9109	-0.0016
0.5149	-0.2348	-0.8244
Ni-Co		
$g^b = 0.60 (3)$	$g = 0.93 (1)$	$g = 2.09 (1)$
-0.5774	0.6807	0.4508
0.7661	0.6427	0.0106
0.2825	-0.3515	0.8925

^a The x, y, z laboratory axes are defined as follows: z is parallel to b ; x is in the ab plane. ^b Estimated standard deviation in parentheses.

EPR Spectra of Ni-Cu Pairs. In cobalt-doped $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, beyond the signals that we attribute to Ni-Co pairs to be described below, also another set of signals that can be attributed to Ni-Cu pairs was detected. A proof of this assumption comes from the fact that in certain crystal orientations a four-line pattern is resolved, which can be attributed to hyperfine interaction with ^{63}Cu and ^{65}Cu . Also the g and A values compare well with those obtained for other Ni-Cu pairs. The angular dependence of the g^2 values in the three experimental rotations is shown in Figure 2. These data were analyzed through the usual least-squares techniques²⁰ to yield the principal g values and directions shown in Table I. Copper hyperfine splitting was resolved only in some crystal orientations. The maximum splitting was observed when the lowest g value was observed. It corresponds to $47 \times 10^{-4} \text{ cm}^{-1}$.

EPR Spectra of Ni-Co Pairs. The single-crystal spectra of cobalt-doped $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ showed the presence of a set of signals that in some crystal orientations yielded an eight-line pattern, which can be attributed to the hyperfine interaction with ^{59}Co . The angular dependence of the g^2 values in the three experimental rotations is shown in Figure 3. The principal g values and directions, obtained with the procedure described above,²⁰ are given in Table I. The ^{59}Co hyperfine was resolved in some angular orientations, but it was not possible to analyze properly the A tensor due also to the limited number of experimental points for which reasonably narrow spectra were obtained. Close to the g_2 and g_3 values, A values of 36×10^{-4} and $84 \times 10^{-4} \text{ cm}^{-1}$ were observed. Some representative spectra are shown in Figure 4.

So that information on the single cobalt(II) ion could be obtained, the powder spectrum of zinc-doped $\text{Co}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ was recorded. It is typical of a cobalt ion in a distorted-octahedral environment, with $g_1 = 1.9$, $g_2 = 2.9$, and $g_3 = 6.3$. Attempts to grow single crystals isomorphous

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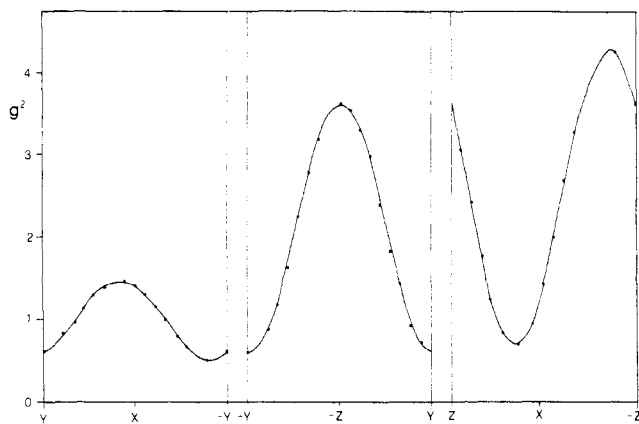


Figure 3. Angular dependence of the g^2 values of the Ni-Co pair in the three experimental rotations (along the axes defined in Table I). The curves correspond to the least-squares fit of the experimental points.

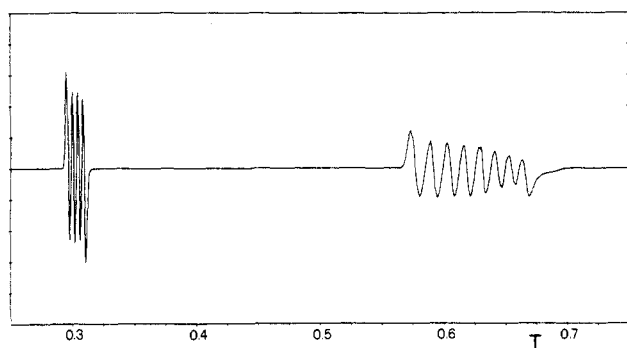


Figure 4. Representative EPR spectrum. The static magnetic field has direction cosines (0.87, 0, 0.5) in the laboratory frame defined in Table I.

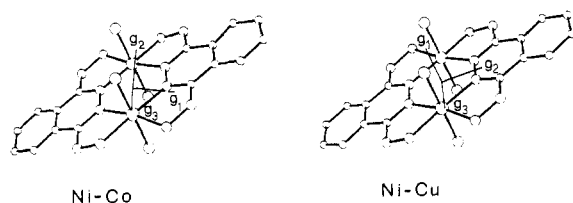


Figure 5. Orientation of the g tensors of the Ni-Cu and Ni-Co pairs within the molecular frames of $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$.

to the nickel analogue were unsuccessful.

Discussion

The orientations of the g tensors of the Ni-Cu and Ni-Co pairs within the molecular frames of $\text{Ni}_2(\text{dhph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ are shown in Figure 5. g_1 of the Ni-Cu pair is closely parallel to the Ni-OH₂ directions,¹⁴ g_3 is very close to the metal-metal direction (4.6°), and g_2 is parallel to the C₂ axis of the phthalazine molecule. In the Ni-Co pair the g directions are not so close to relevant molecular directions. However, g_2 of the Ni-Co pair makes an angle of 17° with g_1 of the Ni-Cu pair, g_1 of the Ni-Co makes an angle of 16° with g_2 of Ni-Cu, and g_3 of Ni-Co makes an angle of 8° with that of Ni-Cu.

It is interesting at this point to compare the g values observed in this case with those previously reported¹⁴ for Ni-Co and Ni-Cu pairs in dinickel(II) bis(1,5-diphenyl-1,3,5-pentane-trionate)-tetrakis(pyridine) (M-M' trik pairs). In that case also the dinuclear complex was formed by two octahedral moieties bridged through two equatorial ligands.^{21,22} The main

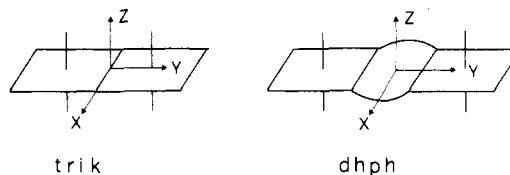


Figure 6. Scheme of the trik and dhph dinuclear complexes.

Table II. Comparison of the g Values of M-M' Pairs in trik and dhph Complexes^a

	trik	dhph
	Ni-Cu	
z	2.15	2.07
x	2.21	2.21
y	2.25	2.25
	Ni-Co	
z	2.1	0.6
x	1.2	0.9
y	0.3	2.1
	Co-Zn	
z	1.9	2.9 ^b
x	6.3	6.6 ^b
y	3.5	1.9 ^b

^a For the exact relation between the g directions and the x , y , and z axes see Table I. ^b Principal directions were assumed according to the discussion in the text.

difference between the present and the previous case is that in the dhph complex the bridge is a polyatomic one, while in the triketonate complex the bridge is monoatomic. The scheme of the two complexes, together with the orientation of the principal axes of a tensor in C_{2v} symmetry, is given in Figure 6. The C₂ axis is labeled as y .

The actual principal directions of g observed for the dhph and trik complexes are not parallel to the x , y , and z axes. In particular, larger deviations are observed for the Ni-Co and Co-Zn pairs and smaller for the Ni-Cu and Cu-Zn pairs. However, in general, the principal directions of g are not too far from the x , y , and z axes, the maximum deviation being 27°. Therefore, it is possible in a first approximation to relate the g_i values to the x , y , and z directions that are closest to them and to compare the results of the trik and dhph complexes, as shown in Table II. The corresponding g values for the Ni-Cu pairs are very close to each other, the only difference being observed in the g_z values. In the Ni-Co pairs on the other hand, although the g values are rather similar, the directions are much different. In fact identical g values of 2.1 are observed for the trik and dhph complexes, but for the latter g is close to y , and for the former it is close to z . In both cases the second largest g value is observed close to x , while the smallest g values are observed in one case close to y and in the other close to z . It is not possible to make a similar comparison for the Co-Zn pairs, since we were not able to grow single crystals of the cobalt complex that are isomorphous to the nickel one.

In a previous paper¹⁴ we used a model, originally suggested by Kahn,¹¹ for calculating the g values of the Ni-Co pair. According to this model the Hamiltonian appropriate to the couple is

$$\hat{H} = \hat{H}_{\text{Co}} + \hat{H}_{\text{Ni}} + \hat{H}_{\text{Ni-Co}} \quad (1)$$

where \hat{H}_{Co} includes the contributions of the low-symmetry ligand field components on the ground $^4\text{T}_{1g}$ manifold, and the spin-orbit coupling, \hat{H}_{Ni} is the zero-field splitting Hamiltonian for the ground level $^3\text{A}_{2g}$ of octahedral nickel(II), and $\hat{H}_{\text{Ni-Co}}$

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is the interaction Hamiltonian. A convenient form^{14,23} for the three Hamiltonians is

$$\hat{H}_{\text{Co}} = -\frac{1}{3}k\gamma\zeta\hat{L}\cdot\hat{S}_1 - D_{\text{Co}}(\hat{L}_z^2 - \frac{2}{3}) - E_{\text{Co}}(\hat{L}_x^2 - \hat{L}_y^2) \quad (2)$$

$$\hat{H}_{\text{Ni}} = D_{\text{Ni}}(\hat{S}_{2z}^2 - \frac{2}{3}) + E_{\text{Ni}}(\hat{S}_{2x}^2 - \hat{S}_{2y}^2) \quad (3)$$

$$\hat{H}_{\text{Ni-Co}} = \hat{J}\hat{S}_1\cdot\hat{S}_2 \quad (4)$$

In (2) k is the Stevens orbital reduction factor,²⁴ ζ is the spin-orbit coupling constant for the cobalt ion, and γ is a number ranging from $-\frac{3}{2}$ to -1 , for taking into account the admixture of the excited $^4T_{1g}$ level into the ground level.²⁵ In (4) \hat{J} is an orbital operator such that

$$\langle \Gamma, i | \hat{J} | \Gamma', j \rangle = J \delta_{\Gamma\Gamma'} \delta_{ij} \quad (5)$$

where $|\Gamma, i\rangle$ is one of the eigenfunctions of $\hat{H}_{\text{Co}} + \hat{H}_{\text{Ni}}$, which transforms as the irreducible representation Γ of the group C_{2v} assumed for the molecule. Since the $^4T_{1g}$ functions in C_{2v} span the B_1 , B_2 , and A_2 irreducible representations and $^3A_{2g}$ transforms as B_1 , three J_{Γ} parameters will be different from zero, namely, J_{A_1} , J_{A_2} , and J_{B_2} . They give the interaction of each split component of $^4T_{1g}$ with the $^3A_{2g}$ nickel(II) state.

The use of the three Hamiltonians (eq 2-4) requires nine parameters, which seem to be too numerous to be adequately determined by the comparison with the three experimental g values. In the case of the trik complexes¹⁴ we were able to reduce the number of parameters by obtaining separate information on the single-ion Hamiltonians, \hat{H}_{Co} and \hat{H}_{Ni} . In the present case we have only polycrystalline powder EPR spectra for the cobalt(II) ion and single-crystal polarized electronic spectra for the nickel(II) ion. In fact we have the spectra of the dinuclear compound, but since J is rather small,¹⁷ it may be safely assumed that the electronic spectra do not differ too much from those of the single ion. With these data we will calculate the relevant parameters of \hat{H}_{Co} and \hat{H}_{Ni} , and then, keeping these parameters fixed, we will try to fit the experimental g values of the Ni-Co pair varying the J_{Γ} parameters.

The single-crystal polarized electronic spectra of $\text{Ni}_2(\text{dph})_2(\text{H}_2\text{O})_4\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ show that the symmetry of the nickel(II) ion is not axial, since at least six peaks are observed in the range 8000–12 000 cm^{-1} . Although one of them might be due to a spin-forbidden transition, all the other peaks seem to be due to genuine spin-allowed transitions, thus exceeding the number of four expected in axial symmetry.

The energies of the electronic transitions were calculated through the angular overlap model,^{27,28} with use of the molecular coordinates seen in the crystal structure of the complex.¹⁷ For the sake of simplicity all the e_{σ} parameters were initially set to zero, and the four nitrogen atoms coordinated in the equatorial plane were considered to be identical. From the calculations it is apparent that the geometrical coordinates alone are able to determine a departure from axial symmetry. For instance with $e_{\sigma}^{\text{N}} = 4367 \text{ cm}^{-1}$, $e_{\sigma}^{\text{O}} = 2167 \text{ cm}^{-1}$ yields the following calculated transitions: $^3A_{2g} \rightarrow ^3T_{2g}$ at 9300, 9500, and 11 700 cm^{-1} ; $^3A_{2g} \rightarrow ^3T_{1g}(\text{F})$ at 15 400, 16 200, and 18 900 cm^{-1} . The splitting of the octahedral levels is apparently dominated by the small N-Ni-N in-plane angle (78° on the average). The g and D tensors can be easily calculated through a perturbation approach, yielding $g_x = 2.17$, $g_y = 2.21$, and $g_z = 2.16$ and $D_{xx} = 0.89 \text{ cm}^{-1}$, $D_{yy} = -3.63 \text{ cm}^{-1}$, and $D_{zz} =$

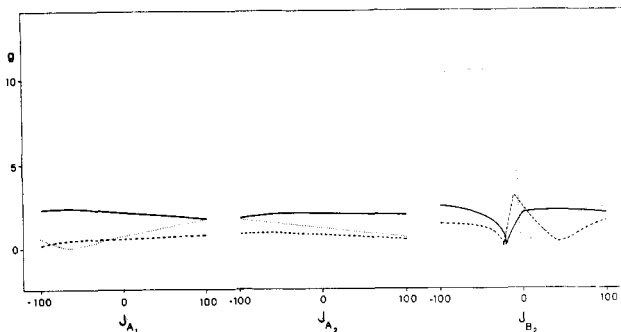


Figure 7. Dependence of the g values on J_{A_1} , J_{A_2} , and J_{B_2} : (---) for g_z ; (—) for g_y ; (···) for g_x .

2.74 cm^{-1} . It is surprising to notice that the largest zero-field splitting component is in the plane of the four nitrogen atoms and not parallel to the nickel-oxygen direction, as one might have anticipated describing the complexes as elongated octahedra. Again the small in-plane bond angles play a major role in determining the ligand field.

A better fit of the transitions was obtained by allowing the phthalazine nitrogen atoms to have $e_{\pi} \neq 0$. The best parameters are as follows: for the phthalazine $e_{\sigma} = 7500 \text{ cm}^{-1}$, $e_{\pi} = 1875 \text{ cm}^{-1}$; for the hydrazine nitrogen $e_{\sigma} = 4500 \text{ cm}^{-1}$, $e_{\pi} = 0$; for water $e_{\sigma} = 3846 \text{ cm}^{-1}$, $e_{\pi} = 1385 \text{ cm}^{-1}$. The calculated energies of the transitions are 9500, 10 200, 12 800, 16 500, 16 700, and 19 900 cm^{-1} . The corresponding spin Hamiltonian parameters are as follows: $g_x = 2.16$, $g_y = 2.24$, and $g_z = 2.15$ and $D_{xx} = 2.49 \text{ cm}^{-1}$, $D_{yy} = -6.45 \text{ cm}^{-1}$, and $D_{zz} = 3.96 \text{ cm}^{-1}$ calculated with $k = 0.75$ and $\zeta = 649 \text{ cm}^{-1}$.

Using the calculated g values for the nickel ion, it is possible to calculate the g values for the copper(II) ion. In fact the g values of the Ni-Cu pair are typical of an $S = \frac{1}{2}$ system,^{27,28} showing that the coupling between the two metal ions is antiferromagnetic. Using the reported formulas,^{29,30} one finds for the copper ion $g_z = 2.39$, $g_x = 2.06$, and $g_y = 2.10$ in fair agreement with what one would expect for a pseudooctahedral complex.³¹ Sample calculations for a copper chromophore with the same geometrical coordinates as the nickel complex yield $g_z = 2.37$, $g_x = 2.06$, and $g_y = 2.08$. The good agreement between the two sets of g values calculated for the copper ion gives an indirect confirmation to the spin Hamiltonian parameters calculated for the nickel ion.

The second step for characterizing the Ni-Co pair is that of fixing the parameters for the cobalt(II) ion. For this purpose we tried to fit the experimental powder spectra with the angular overlap model we have been using for rationalizing the EPR spectra of high-spin cobalt complexes.³² We used the same coordinates and the same parameters e_{λ} obtained from the analysis of the electronic spectra of the nickel complex. The calculated values are in good agreement with the experimental data in regard to both the electronic transitions and the g values. In particular the latter are $g_x = 6.1$, $g_y = 2.0$, and $g_z = 3.4$. What is important is that the smallest g value is calculated close to the y direction. This is rather surprising, since in general in pseudooctahedral cobalt complexes the smallest g value has been experimentally found and confirmed through calculations to be close to the perpendicular to the equatorial plane.³³ Again in this case the small in-plane

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bond angles modify dramatically the ligand field around the cobalt ion. On the basis of the calculated values therefore we assign the experimental g values to the principal directions as shown in Table II.

In order to have the correct parameters for the \hat{H}_{Co} Hamiltonian, we recalculated the g values also within this simplified model. The best fit values are $g_x = 6.1$, $g_y = 2.0$, and $g_z = 3.4$, with the parameters fixed at $\gamma = -1.5$, $\zeta = 533 \text{ cm}^{-1}$, $D_{Co} = -877 \text{ cm}^{-1}$, $E_{Co} = 246 \text{ cm}^{-1}$, and $k = 1$.

The third step was that of calculating, with the parameters for \hat{H}_{Co} and \hat{H}_{Ni} fixed as shown above, the g values of the Ni-Co pair. A 36×36 matrix for the ${}^4T_{1g} \times {}^3A_{2g}$ manifold was calculated, which by diagonalization gave a spectrum of eigenvalues and eigenvectors. The g values within the lowest Kramers doublet were calculated with the Zeeman Hamiltonian:

$$\hat{H}_Z = \mu_B B(k\hat{L}_{Co} + g_e\hat{S}_{Co}) + \mu_B B g_{Ni} \hat{S}_{Ni} \quad (6)$$

The calculated g values for several sets of values of the J_{A_1} , J_{A_2} , and J_{B_2} parameters are shown in Figure 7. It is apparent that the parameter that determines the largest variation of the g values is J_{B_2} . The calculations were performed also with different zero-field splitting parameters of the nickel(II) ion, since in the procedure outlined above they were found to depend to some extent on the angular overlap parameters. The calculated g values of the Ni-Co pair, however, were found to be relatively insensitive to the actual values of D_{Ni} and E_{Ni} used.

The best fit parameters are $J_{A_1} = 30 \pm 10 \text{ cm}^{-1}$, $J_{A_2} = 30 \pm 10 \text{ cm}^{-1}$, and $J_{B_2} = 30 \pm 10 \text{ cm}^{-1}$. The g values computed with these parameters fixed at 30 cm^{-1} are $g_x = 1.0$, $g_y = 2.1$, and $g_z = 0.6$. Comparing them to the values for the trik complexes shows that the J_{A_2} and J_{B_2} parameters are only slightly smaller in the present case, while J_{A_1} is definitely larger. It is worth mentioning that in the nickel dhph complex J was estimated to be 92 cm^{-1} , while it was 30 cm^{-1} in the nickel trik complex.

The A_1 , A_2 , and B_2 pathways are, to a good approximation, determined according to the relations^{34,35}

$$\begin{aligned} J_{A_1} &= \frac{1}{6}(J_{xy,xy} + J_{xy,z^2} + J_{xy,x^2-y^2} + J_{z^2,z^2} + J_{z^2,xy} + J_{z^2,x^2-y^2}) \\ J_{A_2} &= \frac{1}{6}(J_{xy,xy} + J_{xy,z^2} + J_{xy,yz} + J_{z^2,z^2} + J_{z^2,xy} + J_{z^2,yz}) \quad (7) \\ J_{B_2} &= \frac{1}{6}(J_{xy,xy} + J_{xy,z^2} + J_{xy,xz} + J_{z^2,z^2} + J_{z^2,xy} + J_{z^2,xz}) \end{aligned}$$

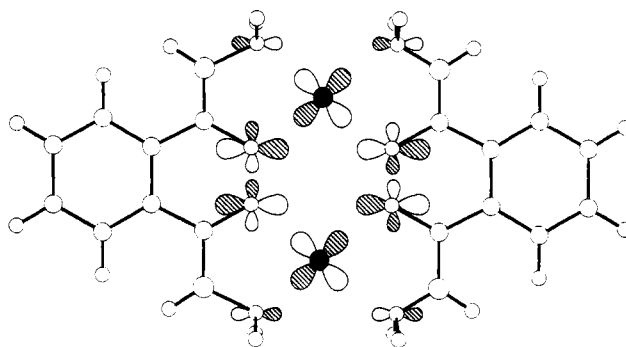


Figure 8. Symmetry of the highest occupied ligand and metal orbitals.

In (7) the first orbital is a nickel orbital, while the second one is a cobalt(II) orbital. Antiferromagnetic contributions are expected only for the couples of orbitals that span the same irreducible representation of C_{2v} symmetry. Therefore only $J_{xy,xy}$, J_{z^2,z^2} , J_{z^2,x^2-y^2} can be effective in determining antiferromagnetic coupling. Extended Hückel calculations on the ligand, for which an idealized C_s symmetry was assumed, show that the highest occupied ligand orbitals have the correct symmetry for determining an antiferromagnetic pathway, as shown in Figure 8. Overlap considerations suggest that the order of the coupling constants is $J_{xy,xy} > J_{z^2,z^2} > J_{z^2,x^2-y^2}$. Of the other exchange interactions J_{ij} the one that may bring some substantial ferromagnetic contribution is J_{xy,x^2-y^2} . As compared to the case of the Ni-Co trik pairs¹⁴ this mechanism, however, should be less effective, because the two orbitals xy and $x^2 - y^2$ are further removed from each other since two metal ions are bridged by two atoms in the dhph ligand, while a monoatomic bridge was present in the trik complex. This might be the reason why in this case the three J values are essentially similar to each other, while in the case of the trik complex the J_{A_1} value, which included the ferromagnetic J_{xy,x^2-y^2} pathway, was substantially smaller than the others.

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Registry No. $Ni_2(dhph)_2(H_2O)_4Cl_4$, 24686-50-8; Cu, 7440-50-8; Co, 7440-48-4.

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EXAFS Study of the Structural Modifications Induced into $MnPS_3$ upon Intercalation

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EXAFS spectra have been recorded at the manganese K edge in the layered compound $MnPS_3$, and in two intercalation compounds containing cobaltocenium cations, at 15 and 300 K. The intercalation process is shown to induce local disorder or distortion in the structural environment of manganese, although the intercalates still have X-ray powder diffraction patterns typical of crystalline materials. These structural effects are discussed in relation to the magnetic properties of the intercalates.

Introduction

Transition-metal hexathiohypodiphosphates MPS_3 , where M is a metal in the +2 oxidation state, form a class of la-

mellar,^{2a} broad-band semiconductors³ with an energy gap lying in the range 1.6–3.5 eV. Their structure² is related to that of $CdCl_2$, with metal ions and phosphorus-phosphorus pairs

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