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ESR Spectra of Nickel(II)–Copper(II) and Nickel(II)–Cobalt(II) Exchange-Coupled Pairs in Transition-Metal Dinuclear Triketonate Complexes

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The ESR spectra of nickel(II)–copper(II) and nickel(II)–cobalt(II) exchange-coupled pairs in bis(1,5-diphenyl-1,3,5-pentanetrionato)tetrakis(pyridine)dimetal(II) (metal = cobalt, nickel) are reported. The metal ions are in octahedral coordination environment so that an orbitally nondegenerate ground state can be anticipated for both nickel(II) and copper(II), but orbital degeneracy is expected for cobalt(II). The ESR spectra show antiferromagnetic interactions for both the pairs studied. For the Co–Ni pair a relatively simple model for exchange between an orbitally degenerate and a nondegenerate ground state was able to reproduce the *g* values.

Introduction

Homodinuclear transition-metal 1,3,5-triketonates have been reported for some time,[1,2] and the nature of the exchange interaction between the metal ions has been investigated. In particular the crystal structure determination of bis(1,5-diphenyl-1,3,5-pentanetrionato)tetrakis(pyridine)dimetal(II)[3,4] (metal = cobalt, nickel), $M_2(DBA)_2(py)_4$, has shown that the metal ions are in octahedral environments, with two oxygen atoms of two triketone ligands acting as bridging donors according to structure **1**. Both complexes are paramagnetic at
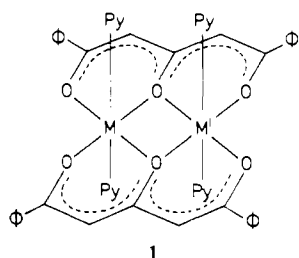
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high temperature, but antiferromagnetic coupling is operative between the two metal atoms.[3,4] For the nickel complex the single ion ground state is orbitally nondegenerate, so that the usual spin Hamiltonian formalism can be applied, and *J* (defined by $\hat{H} = J\hat{S}_1 \cdot \hat{S}_2$) was found to be 30 cm^{-1}. In the case of cobalt no such simplification is possible, since the single ion ground state is orbitally degenerate.

It appeared to us of interest to characterize a cobalt(II)–nickel(II) pair (Co–Ni) in $M_2(DBA)_2(py)_4$, since in this case the exchange interaction is operative between an orbitally nondegenerate ground state and a degenerate one. This appears to be a first step in the direction of establishing some simple model to rationalize the magnetic properties of exchange-coupled orbitally degenerate metal ions.[5-9] We have recorded the ESR spectra of the cobalt–nickel pairs (Co–Ni), as well as of cobalt–zinc (Co–Zn), nickel–copper (Ni–Cu), and copper–zinc (Cu–Zn) pairs, in order to have as much

experimental information as possible on the spin-Hamiltonian parameters of the metal ions.

Experimental Section

The preparation of the $M_2(DBA)_2(py)_4$ complexes (M = Ni, Co) has been described elsewhere.[3,4] The zinc analogue has been prepared with the same procedure. The yellow crystalline material was analyzed satisfactorily. Anal. Calcd: C, 68.79; H, 4.99; N, 8.67. Found: C, 68.66; H, 5.10; N, 8.70.

If in the reaction mixture a little amount of chloride of M′ metal is added to the stoichiometric amount of M chloride, some couples M–M′ are obtained in the M–M lattice. Single crystals suitable for the ESR spectra were obtained from saturated pyridine solutions and oriented on a Perspex rod with the aid of a polarizing microscope. The crystals were kept in a vessel saturated with pyridine, in order to avoid loss of ligand. They were transferred to the ESR spectrometer and the spectra recorded immediately. The crystals of cobalt(II) and nickel(II) complexes were found to conform to the reported structures[3,4] with use of a PW 1100 diffractometer.

Single-crystal ESR spectra were recorded with a Varian E-9 spectrometer equipped with both X- and Q-band frequency (9 and 35 GHz). Liquid-helium temperatures were obtained with use of an Oxford Instrument ESR 9 continuous-flow cryostat.

Results

At liquid-helium temperatures both $Ni_2(DBA)_2(py)_4$ and $Co_2(DBA)_2(py)_4$ are diamagnetic, and no ESR spectra, attributable to monomeric impurities, are observed. Therefore the ESR signals observed when the two complexes are doped with some impurities must be attributed to M–M′ pairs (see below). All the spectra involving nickel and cobalt were recorded at liquid-helium temperature.

(Co, Zn). As previously observed for the mononuclear $Co(acac)_2(H_2O)_2$[10] (acac = 2,4-pentanedione) complex, the ESR signals show evidence of second-order effects in the nonequal spacings of adjacent $\Delta M_I = 0$ hyperfine lines, as well as nuclear quadrupole and/or nuclear Zeeman effects which determine the appearance of forbidden $\Delta M_I = \pm 1$ transitions. The spin-Hamiltonian parameters were obtained through a nonlinear least-squares fit of the experimental $\Delta M_I = 0$ transition fields, using the expressions of the energies previously reported.[12] The least-squares fitting procedure uses the principal values of **g** and **A** and their principal directions with respect to the laboratory axes as parameters. Starting values of the parameters were obtained from a least-squares fitting of the angular dependence of g^2 and g^2A^2, calculated through a first-order analysis, in three orthogonal planes. The corrections on the parameters were estimated by numerical dif-

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Table I. Principal Values and Directions for g and A for the Couples (Co, Zn), (Co, Ni), and (Ni, Co) in $M_2(DBA)_2(py)_4{}^a$

Co, Zn		
$g_1 = 6.27$	$g_2 = 3.50$	$g_3 = 1.87$
-0.7803	0.4958	0.3813
0.3650	-0.1341	0.9213
-0.5079	-0.8580	0.0763
$A_1 = 198 \times$	$A_2 = 38 \times$	$A_3 = 98 \times$
10^{-4} cm^{-1}	10^{-4} cm^{-1}	10^{-4} cm^{-1}
-0.7864	0.5103	0.3480
0.3382	-0.1156	0.9339
-0.5168	-0.8522	0.0817
Co, Ni		
$g_1 = 2.14$	$g_2 = 1.24$	$g_3 = 0.47$
0.3337	-0.7570	0.5618
0.9410	0.3028	-0.1511
0.0557	-0.5791	-0.8134
	$A = 125 \times$	$A = 87 \times$
	10^{-4} cm^{-1}	10^{-4} cm^{-1}
	(19.1°)	(9.8°)
Ni, Co		
$g_1 = 2.10$	$g_2 = 1.23$	$g_3 = 0.38$
0.3470	-0.7767	0.5257
0.9361	0.3213	-0.1432
0.0576	-0.5418	-0.8385
$A = 28 \times$	$A = 127 \times$	$A = 103 \times$
10^{-4} cm^{-1}	10^{-4} cm^{-1}	10^{-4} cm^{-1}
(20.6°)	(19.3°)	(18.9°)

^{a} The direction cosines of the indicated g_i and A_i values are referred to a laboratory reference frame, with y parallel to b and z parallel to the (10$\bar{1}$) direction.
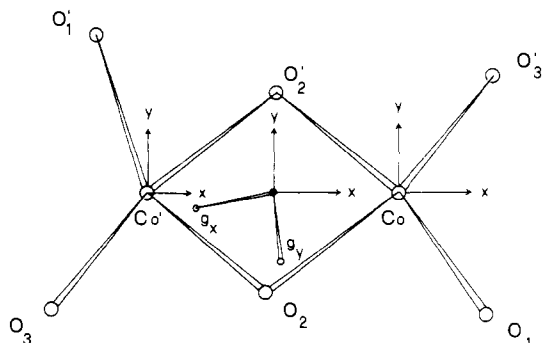

Figure 1. Orientation of the **g** tensors in the molecular frame. g_x corresponds to g_3 of the Co–Ni and Ni–Co pairs and to g_2 of the Co–Zn pair. g_y corresponds to g_2 of the Co–Ni and Ni–Co pairs and to g_1 of the Co–Zn pair. The axial ligands and g_z are not shown for the sake of simplicity.

ferentiation of the computed transition fields with respect to each parameter using standard techniques.[13]

The principal values and directions of **g** and **A** are shown in Table I. The two tensors are parallel within error. They were attributed to one of the two molecules in the cell by using the criterion wherein the g_3 direction is closest to a cobalt–pyridine nitrogen direction. On this basis, the angle of g_3 to Co–N is 10.15°, a value not too dissimilar from that found in Co(acac)$_2$(6-Mequin)$_2$ (6-Mequin = 6-methylquinoline). The projections of g_1 and g_2 in the CoO$_4$ plane are seen to be quite close to the bisectors of the in-plane bond angles. The orientation of the **g** axes in the molecular frame is shown in Figure 1.

(Ni, Co) and (Co, Ni). The ESR spectra seen both in the cobalt lattice in the presence of some nickel impurity and in the nickel lattice in the presence of some cobalt impurity are
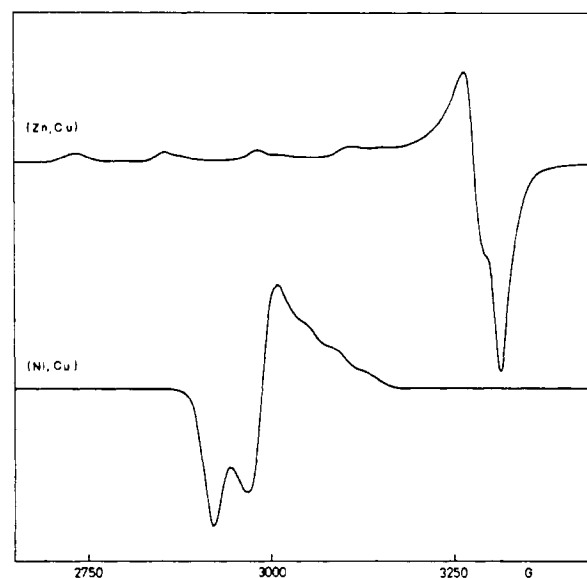

Figure 2. Polycrystalline powder ESR spectra of the Zn–Cu and Ni–Cu pairs at room temperature and 4.2 K, respectively.

completely different from those obtained in the cobalt lattice in the presence of zinc impurities. The signals are at higher fields, as shown by the principal g values shown in Table I. The accuracy in the measurements is not very high, since recording the spectra requires scanning fields ranging from 2500 to 14000 G (1 G = 10^{-4} T), the maximum value which can be reached with our apparatus.

The inaccuracy is particularly serious for the analysis of the A values, so that we prefer to report the hyperfine splitting observed in the experimental setting which are closest to the calculated extremes of **g**. In Table I the angles which are reported in brackets are the angles made by the crystal setting where the A was read and the corresponding principal g direction.

The two sets of g values and directions are very similar to each other, suggesting that they are due to very similar species. We suggest that in both cases they are due to cobalt(II)–nickel(II) couples. We will use the shorthand notation Co–Ni to represent the couple seen in the cobalt lattice and Ni–Co for the couple seen in the nickel lattice.

(Zn, Cu) and (Ni, Cu). The polycrystalline powder ESR spectra of copper-doped Zn$_2$(DBA)$_2$(py)$_4$, (Zn–Cu), and Ni$_2$(DBA)$_2$(py)$_4$, (Ni–Cu), respectively, are shown in Figure 2. The (Zn–Cu) spectra are typical of hexacoordinated copper(II) complexes,[14] with $g_\| = 2.34$, $A_\| = 136 \times 10^{-4}$ cm^{-1}, and $g_\perp = 2.08$. The spectra seen in the nickel lattice are different, yielding $g_1 = 2.25$, $g_2 = 2.21$, $g_3 = 2.15$, and $A_3 = 45 \times 10^{-4}$ cm^{-1}. They can be attributed to (Ni–Cu) couples. At room temperature no signal could be detected; on lowering of the temperature, some broad features could be observed, which eventually became sharp enough to show hyperfine splitting on the lowest g value.

Discussion

The ESR spectra of the pairs involving copper(II) are the simplest to be interpreted. As a matter of fact the g and A values of the Cu–Zn pairs are typical of hexacoordinated[14] copper(II). For Ni–Cu pairs both $S = {}^1/_2$ and $S = {}^3/_2$ spin states can originate through exchange coupling. The g values correspond to a Kramers doublet which must be the ground state of the pair. This might in principle correspond to a $S = {}^1/_2$ spin state or to a $S = {}^3/_2$ largely split in zero magnetic field. However in the latter case at least one g value should

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be larger than 4, if the true g values of the pair are close to 2.

For the $S = {}^1/_2$ state the g values of the pair are expected to be related to the g values of the individual ions according to eq 1.[15,16]

$$g_{Ni-Cu} = {}^4/_3 g_{Ni} - {}^1/_3 g_{Cu} \qquad (1)$$

This relation holds in the assumption that J is the leading term in the Hamiltonian of the pair.

With the observed g values of the Ni–Cu pair, together with those of the Zn–Cu pair for g_{Cu}, the g_{Ni} values are calculated as $g_1 = 2.21$, $g_2 = 2.18$, and $g_3 = 2.20$. In the calculation $g_{3,Ni-Cu}$ was associated to $g_{\parallel,Cu}$, while $g_{1,Ni-Cu}$ was associated to $g_{\perp,Cu}$. The reason for this is that a large hyperfine was observed corresponding to $g_{\parallel,Cu}$ and $g_{3,Ni-Cu}$, suggesting that these values correspond to the z molecular axis. The A_3 value observed for the Ni–Cu pair is close to $^1/_3$ of the $A_{\parallel}$ value of the Zn–Cu pair, as expected.[16,17] The calculated values appear to be very satisfactory for an octahedral nickel(II) chromophore.[14]

In order to have an independent check, we have used an angular overlap approach to calculate the spin-Hamiltonian parameters of an isolated nickel(II) ion in $Ni_2(DBA)_2(py)_4$. The approach is similar to that which we have developed for high-spin cobalt(II),[18] in the sense that the electron repulsion, angular overlap, and spin–orbit coupling perturbations are considered contemporarily by diagonalizing the 30×30 matrix of the spin triplet states. g and D are then calculated with use of a perturbative approach, which for pseudooctahedral nickel(II) should be a reasonable approximation. The input parameters were those obtained from the analysis of the ESR and electronic spectra of the cobalt analogue (see below), since for octahedral complexes it is known that the spectrochemical parameters are very similar for cobalt(II) and nickel(II).[19] The calculated energy transitions are centered at 10 000, 16 000, and 25 000 cm^{-1} in fair agreement with the observed ones (at 9600 and 16 800 cm^{-1}; at higher frequencies a charge-transfer transition hides the d–d bands). The calculated spin-Hamiltonian parameters are $g_x = 2.21$, $g_y = 2.21$, $g_z = 2.23$, $D = -2.63$ cm^{-1}, and $E = -0.58$ cm^{-1}. The maximum zero field splitting is calculated along the axis corresponding to the metal–nitrogen bond direction. The calculated zero field splitting is sufficiently small to ensure that the analysis using relation 1 is correct.

Since the $S = {}^1/_2$ state is lowest in energy for the pair, the interaction between the copper(II) and the nickel(II) ions is antiferromagnetic. For octahedral d^8–d^9 exchange-coupled ions, bridged by two ligands atoms, a very strong antiferromagnetic pathway is provided by the xy metal orbitals (see Figure 1 for the chosen reference frame).[19,20] The extent of coupling is known to depend on the M–O–M' angle,[21,22] which in the present nickel lattice is 101.5°, sufficiently far from 90° to justify antiferromagnetism. Another possible pathway which is present in the Ni–Cu pair is that relative to the xy orbital on copper and z^2 on nickel. This pathway also provides antiferromagnetic superexchange, since both xy and z^2 are σ antibonding relative to the in-plane ligands. Since, however, the squared overlap ratios for xy and z^2 with one in-plane ligand are 3:1, the second pathway is expected to be less effective.

Table II. Experimental and Calculated g and A Values for the Co–Zn Pair

g_{exptl}	$g_{calcd}{}^a$	$10^{-4}A_{exptl},$ cm^{-1}	$10^{-4}A_{calcd},$ cm^{-1}
6.27	6.12	198	165
3.50	3.54	38	41
1.87	1.89	92	105

^{a} The crystal field and AOM parameters used in the calculation are $B = 850$ cm^{-1}, $k = 0.85$, $\zeta = 533$ cm^{-1}, $e_\sigma{}^N = 4222$ cm^{-1}, $e_{\pi s}{}^N = 652$ cm^{-1}, $e_{\pi c}{}^N = 931$ cm^{-1}, $e_\sigma{}^O = 5104$ cm^{-1}, $e_{\pi s}{}^O = 893$ cm^{-1}, $e_{\pi s}{}^O = 638$ cm^{-1}, $e_\sigma{}^{O'} = 4583$ cm^{-1}, $e_{\pi s}{}^{O'} = 802$ cm^{-1}, $e_{\pi c}{}^{O'} = 573$ cm^{-1}, $P = 0.026$ cm^{-1}, and $K = 0.35$.

Our data do not allow us to give any value of J, except for the sign.

The analysis of the ESR spectra of the Ni–Co pairs is more complicated. It is useful to start from the Co–Zn pairs, which provide the single ion spin-Hamiltonian parameters.

The g values may be compared to those obtained for Co-$(acac)_2L_2$ complexes (L = pyridine, 6-methylquinoline, water).[10] The g values of the present complexes are more anisotropic than those of the pyridine and 6-methylquinoline adducts of cobalt acetylacetonate, while they are less anisotropic than those of the water adduct. Comparing the structural parameters of $Co(acac)_2(6\text{-methylquinoline})_2$[23] and of the present complex,[3] major distortions are seen in the in-plane bond angles for the latter, thus justifying the observed larger anisotropy. As a matter of fact, while the O–Co–O angles are 90.7, 90.7, and 89.3 for $Co(acac)_2(6\text{-methyl-quinoline})_2$,[20] they are 106.6, 77.3, and 88.1° for the present complex.[5]

The g values for the Co–Zn pair were calculated with use of an angular overlap approach. The e_λ parameters[24] were chosen very close to those used for $Co(acac)_2(6\text{-methyl-quinoline})_2$,[10] while the geometrical parameters used were those seen in the crystal structure determination.[5] The calculated g and A values are in good agreement with the experimental ones, as shown in Table II, and also the electronic transitions are satisfactorily reproduced.

The calculated principal directions of **g** agree satisfactorily with the observed ones. With the above model it is possible to calculate also the magnetic susceptibility.[25] The calculated μ's at selected temperatures are $\mu_{300} = 4.65$, $\mu_{180} = 4.60$, and $\mu_{77} = 4.46$ μ_B, which must to be compared to the values experimentally determined for the dinuclear cobalt complex[5] of $\mu_{300} = 4.28$, $\mu_{180} = 4.07$, and $\mu_{77} = 3.36$ μ_B, confirming that a moderate antiferromagnetic coupling is operative between the two cobalt ions.

The g values of the Co–Ni and Ni–Co pairs possess within error the same principal directions as the Co–Zn pair. This seems to indicate that in the heteronuclear pair the antisymmetric term of the exchange Hamiltonian[26] which tends to cant the spin is not very important.

The ground state of nickel(II) is orbitally nondegenerate, but the ground state of octahedral cobalt(II) is orbitally degenerate, making the interpretation of the data complicated. It is known that spin–orbit coupling and low-symmetry components leave in every case a Kramers doublet as the ground state of cobalt(II) and the g values are usually considered within an $S = {}^1/_2$ spin Hamiltonian formalism.[27] If this Kramers doublet was well separated from any other excited

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ones, it might be hoped to interpret the g values of the Ni–Co pair considering the coupling of $S_1 = 1$ and $S_2 = \frac{1}{2}$ states. However an analysis similar to that used for the Ni–Cu pairs above fails completely. Therefore the orbital degeneracy of the cobalt(II) ion must be explicitly taken into account.

The main problem occurring in the treatment of magnetic coupling between ions possessing orbital degeneracy in the ground state is that the simple spin-Hamiltonian (HDVV) approach breaks down and the number of the parameters which must be included increases dramatically,[28] largely outweighing the number of experimental data which are available.

As previously observed, the minimum level of complication which may occur is that of the exchange interaction between an ion with orbitally nondegenerate ground state and an orbitally degenerate one. Considering a somewhat similar case of coupling involving an octahedral cobalt(II) ion and a square-planar copper(II) ion, Kahn et al.[29] suggested that the interaction could be taken into account through the spin Hamiltonian[30]

$$\hat{H} = \hat{J}\hat{S}_1 \cdot \hat{S}_2 \qquad (2)$$

where $\hat{J}$ is an orbital operator, such that

$$\langle \Gamma | \hat{J} | \Gamma' \rangle = \delta_{\Gamma\Gamma'} J_\Gamma$$

where Γ and Γ' are symmetry labels for the wave function of the dinuclear unit, obtained as a product of individual ion functions. A somewhat similar approach has been used by Ginsberg et al.[31] for the interpretation of the magnetic susceptibility of iron(II) dimers. The theoretical foundation of such a treatment is not completely analyzed. However the above model appears to be the simplest possible to tackle the magnetic interactions in pairs involving orbitally degenerate ground states, and as such we decided to use it. As a matter of fact it worked reasonably well for reproducing the temperature dependence of the magnetic susceptibility of the cobalt–cobalt pair.[29] In the present case the g values and directions as obtained from single-crystal data should provide a somewhat more stringent test of the model.

The symmetry of the homonuclear pairs is C_i in the lattice,[4,5] so that no symmetry element is left for the heteronuclear pair. However the overall symmetry must not be far from C_{2v} as shown by the principal g directions which are close to the x, y, and z axes of a C_{2v} group (see Figure 1).

The complete Hamiltonian has the form[11,29,32]

$$\hat{H} = \hat{H}_{Co} + \hat{H}_{Ni} + \hat{H}_{Co-Ni} \qquad (3)$$

where

$$\hat{H}_{Co} = -\tfrac{1}{3}k\gamma\zeta\hat{L}\cdot\hat{S} - D_{Co}(\hat{L}_z^2 - \tfrac{2}{3}) - E_{Co}(\hat{L}_x^2 - \hat{L}_y^2) \quad (4)$$

$$\hat{H}_{Ni} = D_{Ni}(\hat{S}_z^2 - \tfrac{2}{3}) + E_{Ni}(\hat{S}_x^2 - \hat{S}_y^2) \qquad (5)$$

$$\hat{H}_{Co-Ni} = \hat{J}\hat{S}_1 \cdot \hat{S}_2 \qquad (6)$$

γ is $-\frac{3}{2}$ in the weak field and -1 in the strong field limit.[33]

The number of the parameters appearing in (3) is large, but we choose to reduce them by considering the single ion g values obtained through our analysis of the ESR spectra of the Co–Zn and Ni–Cu pairs. The method of calculation we employed above uses diagonalization of the complete 40×40 matrix of high-spin cobalt(II) states, while the Hamiltonian (4) is

appropriate for a perturbative approach within the lowest $^4T_{1g}$ level. With the latter the best agreement with the experimental data is found for $D_{Co} = -1120.85$ cm^{-1}, $E_{Co} = -230.39$ cm^{-1}, $\zeta = 533$ cm^{-1}, $k = 0.85$, and $\gamma = 1.5$. With these values the calculated cobalt g values are $g_1 = 5.87$, $g_2 = 3.70$, and $g_3 = 1.97$ in fair agreement with the experiment.

For nickel an isotropic $g_{Ni} = 2.20$ value was assumed, for the sake of simplicity, and D_{Ni} and E_{Ni} are those calculated above. The 12 cobalt(II) functions of the $^4T_{1g}$ level of O_h symmetry together with the three nickel(II) functions give a 36×36 matrix which was diagonalized. The g values of the pair were calculated by applying the Zeeman operator

$$\hat{H}_z = \mu_B B(k\hat{L}_{Co} + g_e\hat{S}_{Co}) + \mu_B g_{Ni} B \cdot \hat{S}_{Ni} \qquad (7)$$

to the ground Kramers doublet obtained by the diagonalization of the above matrix. The only adjustable parameters left are J_{A_1}, J_{A_2}, and J_{B_2}, and they were varied in the range -200 to $+200$ cm^{-1}. The calculated g values are very sensitive to the J values, J_{B_2} being the most important in fixing the g values. The best fit was found for $J_{A_1} = 4 \pm 4$, $J_{A_2} = 45 \pm 5$, and $J_{B_2} = 45 \pm 5$ cm^{-1}. The calculated g values are $g_x = 0.46 \pm 0.5$, $g_y = 1.20 \pm 0.5$, and $g_z = 2.10 \pm 0.5$. The interaction appears to be antiferromagnetic.

It is interesting to note that the calculated J values in the present case are not identical, J_{A_1} being far smaller than the other two, which in turn are pretty close to each other. To a good approximation the unpaired electrons of the nickel(II) can be considered to be in the xy and z^2 orbitals (according to the axes shown in Figure 1), while the orbital parts of the Co(II) wave functions can be written as[29]

$$^4A_2 = \alpha(a_1b_1b_2) - (1 - \alpha^2)^{1/2}(a_1a_1'a_2)$$

$$^4B_1 = \alpha(a_1b_1a_1') - (1 - \alpha^2)^{1/2}(a_1a_2b_2)$$

$$^4B_2 = \alpha(a_1b_1a_2) - (1 - \alpha^2)^{1/2}(a_1a_1'b_2)$$

where a_1 and a_1' denote the A_1 symmetry one electron orbitals of higher and lower energy, respectively. The value of α depends on the value of γ. According to the value of γ, we used $\alpha = 0.89$, so that the components multiplied by $(1 - \alpha^2)^{1/2}$ can be neglected to a first approximation. The values of J will be determined by the coupling between the nickel and cobalt orbitals of appropriate symmetry. The cobalt $^4A_2$ wave function contributes to J_{B_2}, $^4B_1$ to J_{A_1}, and $^4B_2$ to J_{A_2}, respectively. Different exchange pathways are involved for the three J values. For all of them the antiferromagnetic contributions involve the xy and z^2 orbitals on the two centers. Of the possible ferromagnetic pathways one which must be particularly efficient is that involving xy on nickel and $x^2 - y^2$ on cobalt, which appears to be operative in J_{A_1}. If this contribution is sizeable it must tend to decrease the observed J_{A_1} value. As a matter of fact strong ferromagnetic exchange was found for a Cu(II)–VO(IV) pair,[34] and it was attributed to a superexchange pathway involving a $x^2 - y^2$ orbital on copper and xy orbital on vanadyl.

The calculated J values are not much dissimilar from those obtained for the analysis of the temperature dependence of the magnetic susceptibility of Ni$_2$(DBA)$_4$(py)$_4$ ($J = 25$ cm^{-1}),[4] giving some support to the suggested model.

It appears therefore that through the analysis of the ESR spectra of exchange-coupled heterodinuclear pairs it is possible to parameterize the exchange interactions also in the case of orbitally degenerate ground levels. More experiments are under way in order to confirm this possibility.

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