the d_{xz} orbital of the copper is donated to the site 2 nitrogen p_y orbital by 0.01. Table II shows the final results obtained from such calculations. The difference between m and m' reflects the fraction of electrons donated from the copper d^2-hybrid orbitals to the nitrogen p_x orbitals. Then if we further assume that the transferred electrons are shared equally by the carbon and the nitrogen, 0.06 (0.03 × 2) electron moves from the d^2-hybrid orbitals of the copper to the π_x^* orbitals, whereas 0.18 lone-pair electron of the nitrogen moves to the copper sp^2-hybrid orbital through the Cu–N σ bond. Furthermore, 0.01 electron of the d_{xz} orbital of the copper atom is donated to the nitrogen p_y orbital through the Cu–N π bond. From these orbital populations of nitrogen, we can estimate orbital populations of copper to be $u = 1.94$, $N_{d_{xz}} = 1.99$, and $y = 0.18$ using the parameters in Table II.

b. Copper Site. Consideration of the ^{14}N NQR data in the preceding subsection indicates that $u = 1.94$, and $N_{d_{xz}} = 1.99$ should be used in eq 6. Jørgensen's electronegativity data lead to a value 0.76 for x. Furthermore, $q_{zz}(3d)$ and $q_{zz}(4p)$ were calculated by using the Slater-type atomic orbital functions. With all these parameter values combined, the asymmetry parameter η at the Cu site could be obtained as a function of y. Using 0.78 for η, which was determined by Graybeal and McKown, we obtain $y = 0.32$. This value is different from 0.18, which was determined in the preceding subsection. The discrepancy is small but reflects the inadequacy of certain assumptions such as the adoptation of the Slater-type functions, which are not very accurate at the nuclear position.

Conclusion

In view of the limitations of the present analysis, which are obvious from assumptions involved, we cannot carry the discussion too far. However, all the intriguing features of the experimental results have been accounted for satisfactorily. In particular, the remarkable positive temperature coefficient of the resonance frequency of Cu has been found to be due to weakening of d–π^* bonds between Cu and C atoms as a result of increasing vibrational amplitude.

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Contribution from the General Chemistry Institute,
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Magnetic Resonance Spectra of a Heterodinuclear (Ni–Co) Metal Complex

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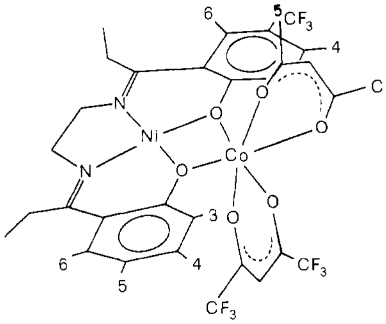
The single-crystal EPR spectra of the $Ni(prp)_2enCo(hfa)_2$ complex ($(prp)_2en$ is the Schiff base formed by 2-hydroxypropiophenone and ethylenediamine; hfa is hexafluoroacetylacetonate) have been recorded at 4.2 K. Since the nickel(II) ion is in a square-planar environment and the cobalt(II) ion in an octahedral one, the EPR spectra are typical of high-spin cobalt(II) with $g_1 = 2.23$, $g_2 = 3.11$, $g_3 = 6.83$, $A_1 \simeq 150 \times 10^{-4}$ cm^{-1} $A_2 < 30 \times 10^{-4}$ cm^{-1}, and $A_3 \simeq 380 \times 10^{-4}$ cm^{-1}. Also the proton magnetic resonance spectra of acetone-d_6 solutions of the complex have been recorded at room temperature. The isotropic shifts of the aromatic protons are most unusual since all of them are upfield. A possible explanation of this behavior is offered. The spin-Hamiltonian parameters have been compared with those of similar adducts. The implications for the exchange mechanism with paramagnetic ions are considered.

Introduction

The copper(II) and nickel(II) complexes with the tetradentate Schiff bases formed by salicylaldehyde and aliphatic diamines are known to be able to act as bidentate ligands toward transition-metal complexes, yielding dinuclear species.[1-3]

In particular Drago et al.[4] studied the reactions of Co(SALen) and the Cu(SALen) (SALen is the Schiff base formed by salicylaldehyde and ethylenediamine) with metal hexafluoroacetylacetonates ($M(hfa)_2$) and found that starting either from Cu(SALen) and adding $Co(hfa)_2$ or from Co(SALen) and adding $Cu(hfa)_2$ the final product was the same, i.e., Cu(SALen)Co $(hfa)_2$. A kinetic study showed also the mechanism of the exchange of the two metal ions between the two coordination sites.[5]

A related series of complexes have been structurally characterized by Sinn et al.,[6] who used the $M(prp)_2en$ complex as the bidentate ligand instead of M(SALen), $(prp)_2en$ being the Schiff base formed by ethylenediamine with 2-hydroxypropiophenone. They reported the crystal structure determination of $M(prp)_2enM'(hfa)_2$, where M = Cu or Ni and M′ = Mn, Co, Ni or Cu, and found that the coordination environment remains largely constant throughout the series, with the exception of the Ni–Cu complex. A sketch of the dinuclear complexes is shown by **1**.



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We are interested in the characterization of the electronic structures of heterodinuclear complexes,[7-9] with a particular

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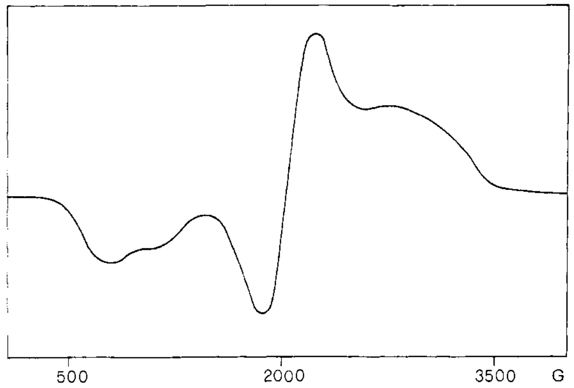

Figure 1. Polycrystalline powder EPR spectrum of $Ni(prp)_2enCo(hfa)_2$ recorded at 4.2 K and 9 GHz.

impetus on the mechanism of magnetic-exchange interactions. It appeared to us of interest to study the series of complexes reported by Sinn,[6] since they offer the possibility to relate the variation in the exchange interactions to the structural parameters and the nature of the metal ions. The EPR spectra of the Ni–Mn and Cu–Mn spectra have been reported previously,[10] and we wish to report here the EPR and proton magnetic resonance spectra of $Ni(prp)_2enCo(hfa)_2$. The EPR spectra are a very sensitive tool to monitor the electronic structures of octahedral high-spin cobalt(II) complexes,[11] detailed knowledge of which is necessary in order to understand the mechanism of exchange in which the metal ion may be involved.[12] The NMR spectra on the other hand should provide some insight into the mechanism of interaction of the cobalt(II) ion with the complex ligand.

Experimental Section

$Ni(prp)_2enCu(hfa)_2$, $Ni(prp)_2enNi(hfa)_2$, and $Ni(prp)_2enCo(hfa)_2$ complexes were prepared as previously reported.[6] Single crystals of the Ni–Co complex were grown by slow evaporation of dichloromethane–methanol solutions and oriented through X-ray analysis.

The $Ni(SALen)Co(hfa)_2$ complex was prepared according to reported procedures.[2]

EPR spectra were recorded with a Varian E-9 spectrometer equipped with an Oxford Instruments ESR9 continuous-flow cryostat.

Proton NMR spectra were recorded with a Varian EM 390 spectrometer in the HR mode.

Results

EPR Spectra. The polycrystalline powder EPR spectrum of the Ni–Co complex recorded at 9 GHz and 4.2 K is shown in Figure 1. It can be interpreted with use of an effective $S = {}^1/_2$ spin Hamiltonian to give $g = 6.5$, $g_2 = 3.2$, and $g_3 = 2.2$. The high- and low-field features are very broad, and we interpret them as due to unresolved metal hyperfine coupling in the magnetically nondilute complex. A spectrum similar to the present one is given also by $Ni(SALen)Co(hfa)_2$, whose structure is not known but presumably is similar to that of $Cu(SALen)Co(hfa)_2$,[4] $Cu(SALen)Cu(hfa)_2$,[2,3] and $Ni(prp)_2enCo(hfa)_2$.[6] The g values are $g_1 = 6.2$, $g_2 = 3.1$, and $g_3 = 2.3$. On the lowest field feature the ^{59}Co hyperfine splitting is better resolved and it is about 260×10^{-4} cm^{-1}.

The single-crystal spectra were recorded at 4.2 K by rotating around to a, b, and c^* crystal axes. In several orientations the metal hyperfine was clearly resolved, confirming the above interpretation of the powder spectra. The angular dependence of the g_2 values is shown in Figure 2. The usual Schonland[13] analysis of the experimental data yielded the principal g values and directions, shown in Table I. Second-order corrections to the g values might be required due to the large and anisotropic cobalt hyperfine constants; however since the resolution of the spectra was not accurate enough, no second-order analysis was attempted. On the other hand it is not expected to give corrections larger than 0.1 on g, which is essentially our experimental uncertainty. The low resolution of the spectra did not allow any analysis of the cobalt hyperfine data; however the A_1 and A_3 constants can be estimated to be $\sim 150 \times 10^{-4}$ and $\sim 380 \times 10^{-4}$ cm^{-1}, respectively, from the experimental spectra, which were recorded close to the extreme g_1 and g_3 values.

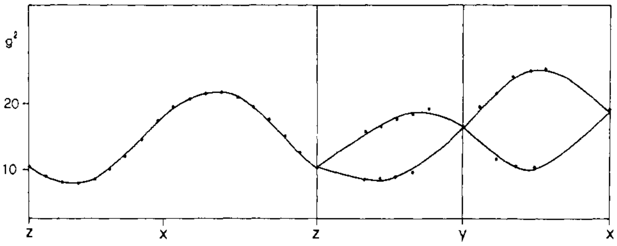

Figure 2. Angular dependence of the g^2 values of $Ni(prp)_2enCo(hfa)_2$ in the laboratory axis frame. $X \equiv c^*$; $Y = b$; $Z \equiv a$. The dots are the experimental points, and the curves are the least-squares fitting of a Schonland analysis.

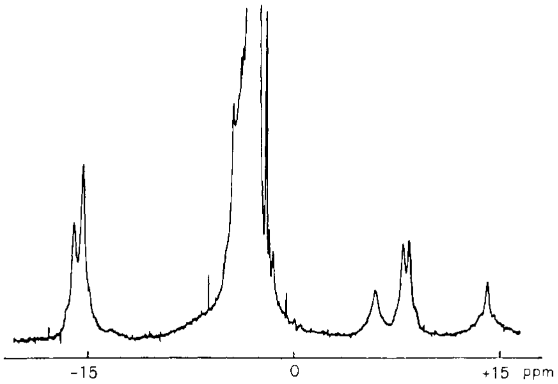

Figure 3. ^1H NMR spectrum of a $(CD_3)_2CO$ solution of $Ni(prp)_2enCo(hfa)_2$ at room temperature.

Table I. Principal g Values and Directions of $Ni(prp)_2enCo(hfa)_2$[a]

	l_{c*}	l_b	l_a
$g_1 = 2.23$	±0.4017	−0.0600	±0.9138
$g_2 = 3.11$	±0.5728	0.7951	±0.1995
$g_3 = 6.83$	±0.7146	0.6036	±0.3537

[a] The l_{c*}, l_b, and l_a values are the direction cosines of the g value with the indicated crystal axes.

NMR Spectra. The proton NMR spectrum of the Ni–Co complex in $(CD_3)CO$ is shown in Figure 3. There are four signals that are upfield from the diamagnetic reference; two signals are downfield, while there is some evidence of at least one signal partially hidden by the signal of the solvent.

For the assignment we started from the diamagnetic $Ni(prp)_2en$ complex and added increasing amounts of $Co(hfa)_2 \cdot 2H_2O$. The signals are seen to move gradually from the diamagnetic position, showing that the complex ligand is exchanging fast on the NMR time scale. This result shows the lability of the Ni–Co complex since in general bidentate ligands are not exchanging fast.[14] The aromatic proton signals

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Table II. Isotropic Shifts of the Aromatic Protons in $Ni(prp)_2enCo(hfa)_2$[a]

proton	3	4	5	6
isotropic shift	+13.7	+15.5	+15.4	+22.1

[a] All the shifts are in ppm. For the numbers see the scheme given by 1.

Table III. Principal g and A[a] Values for Polyketonate Co(II) Complexes

	g_1	g_2	g_3	A_1	A_2	A_3	ref
$Co(acac)_2(6\text{-Mequin})_2$[b,c]	1.9	4.1	5.7				11
$Co(acac)_2(H_2O)_2$[b]	1.9	2.7	6.8	39	20	180	11
(Co,Zn)(trik)py[d]	1.9	3.5	6.3	98	38	198	11
Ni–Co	2.2	3.1	6.8	150		380	*e*

[a] A values are in $10^{-4} \times cm^{-1}$. [b] acac = acetylacetonate. [c] 6-Mequin = 6-methylquinoline. [d] trik = 1,5-diphenyl-1,3,5-pentanetrionate. [e] Present work.

are clearly shifted *upfield*, the 6-proton being the most shifted, followed by the 5-, 4-, and 3-protons in order. The assignment of the aromatic proton resonances in the diamagnetic nickel(II) complex was performed by recording the spectra of ring-substituted derivatives. By weighing the added cobalt complex, it was possible to evaluate the shifts of the dinuclear complex and a formation constant of 2.4×10^4 in fair agreement with the value previously reported for the analogous Cu(SALen)-$Co(hfa)_2$ complex.[5] The isotropic shifts for the aromatic protons in the pure complex are shown in Table II. The assignment for the 5-proton was confirmed by the spectra of the methyl analogue.

For comparison purposes an attempt was made to record also the spectra of the $Ni(prp)_2enCu(hfa)_2$ complex and it was found that reasonably narrow signals could be obtained despite the long electronic spin–lattice relaxation time of the copper(II) ions. Since the EPR spectra show evidence for dynamic Jahn–Teller distortions,[15] the possibility of observing the NMR signal may be due to fast crystal field modulation induced by the Jahn–Teller distortion. Also in this case all the aromatic protons were seen to shift upfield. Among the aromatic protons the largest shift (+189 ppm) was observed for the 3-proton, which yields also the broadest signal. The isotropic shifts of the other protons are much smaller. Spectra were recorded also for the Ni–Ni derivative, but they are difficult to analyze since most of the signals are seen under the envelope of the solvent signals. Only the 3-proton is clearly resolved, with an upfield shift of 17.1 ppm. No signals were found downfield from the diamagnetic aromatic protons.

Discussion

The g values of $Ni(prp)_2enCo(hfa)_2$ and Ni(SALen)Co-$(hfa)_2$ can be compared with those of several base adducts of cobalt(II) acetylacetonate[11] and of dinuclear triketonate complexes previously reported,[17] and these are shown in Table III. The present compounds can be considered as cis adducts of the diketonate complexes, while all the others are trans adducts.

Although the anisotropy in the present compounds is large, it is slightly smaller than that observed in the water adduct.[11] In fact if the two highest g values are considered as the split components of $g_\perp$, then the anisotropy $A = 2(g_x - g_y)/(g_x + g_y)$ is 0.32 for 6-Mequin (6-Mequin = 6-methylquinoline), 0.86 for H_2O, and 0.68 and 0.67 for the present compounds, not very far from the value of 0.57 observed for the other dinuclear complex.[17] Another difference between the two sets of g values, i.e., that of trans adducts and the present cis adducts, is apparent in the lowest g value, which is in every case close to 1.9 for all the trans adducts, while it is distinctly larger than 2 for the present complexes.

Another large difference is observed in the ^{59}Co hyperfine coupling constants. For the trans adducts, the largest value, 190×10^{-4} cm^{-1}, is observed in correspondence with the highest g value,[11] with the second one seen where g is minimum. For the present complex the order of the A values is similar to that for the trans adducts, but the values are distinctly larger. In particular A_1 for the Ni–Co complex is among the largest ever reported for high-spin cobalt(II).[18] Also A_3 appears to be fairly large.

Another comparison can be made on the principal directions. In the trans adducts g_3 is in every case close to the axial bonds, while g_1 and g_2 are in the equatorial plane. The actual directions of the lowest g components depend on the axial ligands, and they were found parallel to the bond directions in the 6-Mequin adduct,[11] at an angle of ~20° in the water adduct,[11] and close to the bisectors in the dinuclear complex.[17]

In the present Ni–Co compound the cell is monoclinic; therefore the assignment of the experimental **g** tensor to the two magnetically nonequivalent molecules is not straightforward. Both the possible sign choices set g_3 close to the Co–O_4 and Co–O_2 bond directions. If the upper signs are used, g_1 is close to the Co–O_1 and Co–O_6 bond directions, while g_2 is close to Co–O_3 and Co–O_5. If the lower signs are used, g_2 is close to Co–O_1 and Co–O_6, while g_3 is not close to any relevant bond direction. However in both choices the axes of the **g** tensor do not make on the average angles smaller than 20° with the bond directions. This is not unexpected since the bond directions are by no means orthogonal to each other. However for a cis adduct one would have expected a principal direction close to the bisector of the angle formed by the oxygen donors of the complex ligand and the cobalt ion. In the isomorphous Ni–Mn complex the zero-field splitting tensor was found to have its z axis parallel to this direction.[10]

An analysis with the AO model we have been using with some success for other high-spin cobalt(II) complexes[19–21] appears to be fairly complicated, since the number of required parameters is very high. We first attempted to use the minimum set of parameters by using only e_σ for each donor atom. The e_σ values for O_1, O_3, O_4, O_5, and O_6 were considered to be equal to each other, due to the similarity of these Co–O bond distances,[6] while e_σ for O_2 was taken smaller, since Co–O_2 is the longest bond in the chromophore.

Although the calculated g values are not too far from the experimental ones ($g_3 = 2.15$, $g_2 = 2.54$, $g_1 = 6.99$) the calculated principal directions are in complete disagreement with the observed ones. In fact the g_1 value is calculated close to the bisector of the chelate complex ligand, in agreement with the expectations but in contrast with experiment. So that the minimum possible complication might be introduced, an attempt was made to transfer to the present compound the e_σ and e_π values we calculated for the trans adducts.[11,17] Again although some agreement was found for the electronic transitions and the g values, the principal directions were in serious disagreement with the experiment. We did not pursue further the attempt to calculate the **g** tensor, since the number of required parameters would be too high. Sample calculations allowing for anisotropic π interactions however showed that

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large rotations of the calculated **g** tensor can be expected.

Also the proton NMR spectra provide some surprise. In fact *all* the aromatic protons are shifted upfield while for all the aromatic systems investigated so far[22] either all the protons have been downfield[23-26] or alternate up- and downfield shifts have been reported.[27-32] These patterns have been attributed essentially to the direct σ and to the π delocalization mechanisms respectively.

In particular for salicylaldiminates[31-35] it was found that the 3- and 5-protons shift upfield, while 4 and 6 shift downfield. In the present case there are some important differences within the salicylaldiminate ligand since it is not acting as a bidentate toward the paramagnetic metal atom as is always the case in simple monomeric complexes. In fact in Ni–Co only the phenolic oxygen atom is bound to the paramagnetic ion, and this apparently determines a different delocalization pattern. This difference and the comparison of the isotropic shifts in simple monomeric complexes with salicylaldimines[31-35] and arylamines[36,37] show that in the normal salicylaldiminates the spin delocalization into the aromatic ring must be determined by the spin density transferred through the nitrogen donor atom. In fact it was previously observed that the isotropic shift patterns in metal complexes with salicylaldimine and arylimine ligands are extremely similar.[37] Also the observation that arylamine complexes show a downfield bias[37] when compared to the salicylaldimine complexes may now be justified by the fact that in the former there is no contribution of spin delocalization through the oxygen donor, which determines an upfield shift as shown by the present spectra.

Trying to explain the delocalization mechanism is more difficult and intriguing. However the fact that no alternation in sign is observed suggests a σ mechanism.[22] This requires attenuation of the shifts for protons that are farther removed from the paramagnetic center, i.e., the expected order of the shifts should be $3 > 4 > 5 > 6$. In the Ni–Cu complex the 3-proton is the broadest and most shifted, while for Ni–Co the pattern is reversed, but some substantial dipolar shift may be anticipated in the latter case as shown by the anisotropic EPR spectra. On the other hand it does not seem to be very helpful to the actual values of g observed in the EPR experiment to calculate dipolar shifts because for high-spin cobalt(II) the susceptibilities would be required.[38] Further the averaging process that occurs in solution, where the complex ligand is in the fast-exchange region with the Co(hfac)$_2$ complex, also makes approximate computations extremely difficult.

Therefore we might conclude that an indirect σ mechanism is operative in the present case. This means that the unpaired electrons are fed into an oxygen orbital, which is essentially orthogonal to the σ system of the aromatic ring. On the other hand little π unpaired spin density is delocalizated into the ring in accordance with previous observation of the π-shielding nature of oxygen atoms.[23]

If this interpretation is correct therefore the bond interaction of the cobalt ion with the complex ligand is essentially σ. However it must be kept in mind that also in the case of pyridine complexes,[26] where an essentially σ mechanism of delocalization of unpaired spin density is agreed upon at present, with minor π contributions, e_π values different from zero are required for the interpretation of the electronic and EPR spectra.[29]

The present data have shown that the electronic structure of the Ni(prp)$_2$enCo(hfa)$_2$ complex is fairly complex, so that a detailed interpretation of the exchange interactions that are operative in Cu(prp)$_2$enCo(hfa)$_2$ seems to be extremely difficult. In particular it appears that simple magnetic orbital models[12,17] must be improved to higher sophistication levels to understand the mechanism of exchange interactions.

Acknowledgment. Thanks are expressed to Professor L. Sacconi for allowing us to record the magnetic resonance spectra and to Mr. Innocenti and S. Vasacci for technical assistance.

Registry No. Ni(prp)$_2$enCo(hfa)$_2$, 69089-20-9.

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