absence of coupling in four-bond systems cannot be used to assume it would not occur in five-bond systems.

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Registry No. I·$CH_3CO_2C_2H_5$, 77629-55-1.

Supplementary Material Available: A listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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EPR Spectra and Zero-Field Splitting of Exchange-Coupled Copper(II)-Manganese(II) Pairs

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In the last few years the exchange interactions of heterodinuclear transition-metal complexes have started to be intensively investigated[1-6] and some relations between the spin Hamiltonian parameters of the individual ions and those of the pairs have been verified. In particular the **g** and **A** tensors could be satisfactorily related to those of the individual ions.[7-9] Fewer data are available for the zero-field splitting tensor, **D**, and this is unfortunate, since D is a relevant parameter in the analysis of the EPR spectra, and it yields in principle information also on the exchange and dipolar coupling.[10]

It appeared to us of interest to study some systems where the zero-field splitting tensor of both the individual ion and the pair could be measured, with the purpose to check if it is also possible to predict for **D** the values of the pair knowing those of the individual ions or vice versa.

Recently Sinn reported[11] the crystal and molecular structure and the magnetic properties of $M(prp)_2enM'(hfa)_2$ where $(prp)_2en$ is the Schiff base formed by 2-hydroxypropiophenone and ethylenediamine, hfa is hexafluoroacetylacetonate, M = Ni and Cu, and M′ = Mn, Co, Ni, and Cu. The $M(prp)_2en$ moiety is square planar, so that, when M = Ni, it is diamagnetic (Figure 1). Therefore the EPR spectra of $Ni(prp)_2enMn(hfa)_2$, Ni-Mn, should provide the spin Hamiltonian parameters of the individual manganese ion. On the other hand the exchange coupling in $Cu(prp)_2enMn(hfa)_2$, Cu-Mn, was evaluated to be $J = -26\ cm^{-1}$, J being defined through the Hamiltonian $\hat{H} = J\hat{S}_1\cdot\hat{S}_2$. This means that the spins of Cu, $S_1 = {}^1/_2$, and of Mn, $S_2 = {}^5/_2$, couple to give two states, $S = 2$ and $S = 3$ separated by $\sim 78\ cm^{-1}$, the quintet state lying lower. The variable-temperature EPR spectra of the Cu–Mn complex therefore should allow one to determine the spin-Hamiltonian parameters of both the $S = 2$ and $S = 3$ states of the pair and compare to those of the $S = {}^5/_2$ of manganese and $S = {}^1/_2$ of copper(II).

Experimental Section

Ni-Mn and Cu-Mn were prepared as previously described.[11] Single crystals were grown by slow evaporation of dichloromethane/methanol solutions. They were found to conform to the reported crystal structures[11] and were oriented by X-ray diffraction techniques. EPR spectra at X (9 GHz) and Q band (35 GHz) were recorded with a Varian E-9 spectrometer equipped with Oxford Instruments ESR 9 and ESR 35 continuous-flow cryostats for low-temperature measurements. The single crystals were mounted on a Perspex rod and rotated by means of a goniometer. Perspex wedges were used to change the orientation of the crystal on the rod.

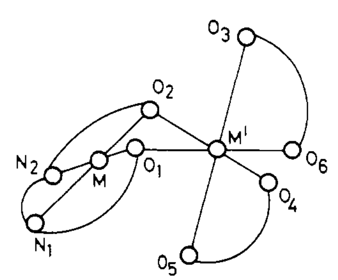

Figure 1. Sketch of the $M(prp)_2enM'(hfa)_2$ complexes.

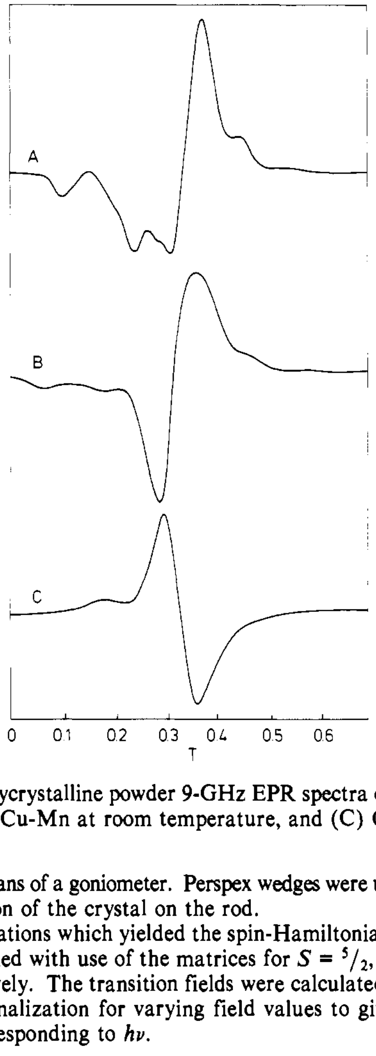

Figure 2. Polycrystalline powder 9-GHz EPR spectra of (A) Ni-Mn at 77 K, (B) Cu-Mn at room temperature, and (C) Cu-Mn at 4.2 K.

The calculations which yielded the spin-Hamiltonian parameters were performed with use of the matrices for $S = {}^5/_2$, $S = 2$, and $S = 3$, respectively. The transition fields were calculated by complete matrix diagonalization for varying field values to give transitions energies corresponding to $h\nu$.

Results and Discussion

Ni-Mn. The polycrystalline powder EPR spectra (Figure 2) of Ni-Mn were recorded at both X- and Q-band frequency, in the temperature range 77–300 K. They are substantially independent of temperature and are typical[12,13] of low-sym-

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metry manganese(II) ions in the presence of a zero-field splitting of the order of 0.05 cm^{-1}.

The single-crystal spectra were recorded by rotating around the *a*, *b*, *c** axes of the unit cell, respectively. The lines are pretty broad and show evidence of unresolved hyperfine splitting, presumably due to intermolecular exchange interactions. The transition fields show the maximum spread in the (001) plane, when the static magnetic field makes an angle of ±45 ± 10° with the *a* and *b* axes. In this angular setting there is good correspondence with the transition fields of the powder spectra. By tilting the crystal on the Perspex rod by means of Perspex wedges, it was confirmed that the transition fields are actually in an extreme.

Five transitions are detected, and we assigned them to molecules with their *z* axes parallel to the magnetic field. The *z* axis of one molecule in the monoclinic cell is therefore almost orthogonal to that of the other magnetically nonequivalent molecule. As a consequence, when a molecule has its *z* axis parallel to the field, the other has the field in the *xy* plane. However we do not find along the extreme spectrum any other transition which can be attributed to the other molecule; therefore the parallel and perpendicular spectra must be almost coincident. This can occur in the case of large anisotropy. As a matter of fact, for $E/D = {}^1/_3$, which corresponds to the maximum possible anisotropy, the resonating fields are identical along both *y* and *z*. If this is the case, the spectrum along *x* must show many coinciding transitions in the region of $g = 2$. Since *y* and *z* are to a good approximation in the (001) plane, *x* for the two molecules must be close to *c**, and in fact in this orientation only transitions close to $g = 2$ are detected.

We confirmed these observations through the calculations described in the Experimental Section, which yielded $D = 0.049 \pm 0.005$ cm^{-1}, $E/D = 0.26 \pm 0.06$, and $g = 2.00$. These values compare well with those reported for a trans-octahedral manganese(II) complex.[14] The principal directions are such that the *x* axis is close to the Ni–Mn direction, which would correspond to the C_2 axis if the chromophore were regular cis octahedral, while the *y* and *z* axes are close to the O_3–Mn–O_5 and Mn–O_4 directions (27 and 34°, respectively).

Cu-Mn. The Cu-Mn EPR spectra are temperature dependent, as shown by the room- and liquid-helium-temperature data reported in Figure 2. Some of transitions are present in the whole temperature range, while some others are present only at high temperature. At 4.2 K it is expected to have only the spectrum of the $S = 2$ state, since with the observed *J* value the intensity ratio I_2/I_3 is 10^4 at this temperature.

The single-crystal spectra at 4.2 K show an angular dependence which is similar to that of the Ni-Mn complex, suggesting that the principal axes of *D* are equally oriented in the two cases. Also in this case the maximum spread of the transition fields is observed in the (001) plane when the static magnetic field is making an angle of ±45 ± 10° with the *a* and *b* crystal axes. The minimum spread on the other hand is observed when the static magnetic field is parallel to *c**. In the spectrum corresponding to the maximum spread four transitions are observed in accord with the assignment to the $S = 2$ multiplet.

The spin-Hamiltonian parameters were calculated to be $D = 0.034 \pm 0.004$ cm^{-1}, $E/D = 0.28 \pm 0.03$, $g_x = 2.00$, $g_y = 2.00$, and $g_z = 1.96$. The *g* values were estimated by using the corresponding values for Cu(prp)$_2$en[15] and the reported relations.[8]

The spectra at room temperature contain more transitions; some of them corresponding to the low-temperature spectra are attributed to the $S = 2$ multiplet and the others to the $S = 3$ state. The expected intensity ratio I_2/I_3 is ~1.5 at 300 K.

The angular dependence of the transitions corresponding to $S = 3$ is similar to the previous ones in the sense that the maximum spread is again observed in the (001) plane, at the same angular setting. The spectrum along *c** however is by no means close to isotropic in this case. On the contrary the resonant fields are close to the maximum spread values. In the spectra where the maximum spread is observed in the (001) plane a rather intense signal shows up at $g = 2$ which cannot be attributed to the $S = 2$ state, since no such transition is observed at low temperature. We interpret these data as indicative of the fact that the *D* directions are still more or less in the same positions and that the anisotropy is large but that the sign of the *E*/*D* ratio has been reversed and that the almost isotropic spectrum now shows up parallel to *y* instead than to *x*.

The spin-Hamiltonian parameters were calculated to be $D = 0.047 \pm 0.005$ cm^{-1}, $E/D = -0.23 \pm 0.02$, $g_x = 2.01$, $g_y = 2.01$, and $g_z = 2.04$. The *g* values were calculated as for the $S = 2$ state, allowing for the different coupling coefficients.

Comparison of the Spin-Hamiltonian Parameters. In the Cu–Mn complex the coupling of the spins through the exchange interaction determines the zero-field splitting parameters. Since *J* is much larger than all the other interactions the **D** tensors of the $S = 2$ and $S = 3$ states are related to the tensor of the $S = {}^5/_2$ state of manganese, $\mathbf{D}_{Mn}$, according to the eq 1 and 2,[8,16-18] where D_e and D_d are the anisotropic

$$S = 2 \qquad D = {}^4/_3D_{Mn} - {}^1/_6D_d - {}^1/_6D_e \qquad (1)$$

$$S = 3 \qquad D = {}^2/_3D_{Mn} + {}^1/_6D_d + {}^1/_6D_e \qquad (2)$$

components of the exchange and magnetic dipolar Cu–Mn interactions, respectively. To obtain eq 1 and 2, it was considered that the principal axes of *D* in the $S = {}^5/_2$, $S = 2$, and $S = 3$ states remain parallel. D_d is expected to have its principal axis parallel to the Cu–Mn direction, therefore to a good approximation parallel to D_{xx} of the isolated manganese ion. The numerical value of D_d is calculated to be 0.0065 cm^{-1} while $E/D = 0.05$.

D_e is less easily taken into consideration, but its principal axes are expected to be dominated by the copper *g* anisotropy.

According to eq 1 and 2 the sum of the *D* values for the $S = 2$ and $S = 3$ states, respectively, should be equal to twice the *D* value of manganese. The observed values however are not in agreement with this prediction, the sum being smaller by about 15–20%. This results might be indicative of exchange striction effects, which were kept responsible for the observed deviation of the observed parameters from the expected ones in Mn–O–Mn pairs.[19] Also the antisymmetric exchange[20] might be involved in the mechanism. It appears therefore that the good agreement between the observed values of *g* and *A* of the Cu–Mn pairs and those calculated with use of the isolated copper and manganese values[7-9] does not apply to the zero-field splitting tensor.

The present data however have shown that the principal axes of the **D** tensors of the isolated ion and of the pair are essentially parallel and that the *D* and *E* values remain quite similar.

Registry No. Ni-Mn, 69069-41-6; Cu-Mn, 69089-19-6.

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