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Pyrazoles and Imidazoles as Ligands. X.[*] Electron Paramagnetic Resonance Spectra of Mn^{II} in a Tetragonal Environment of four Pyrazoles and two Anions

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Electron Paramagnetic Resonance Spectra have been recorded for some compounds of the type $Mn(ligand)_4(anion)_2$*, with pyrazole and 3(5)-methyl pyrazole as the ligands, and* Cl^-, Br^-, I^-, *and* NO_3^- *as the anions.*

The spectra show absorptions far from $g_{eff}=2$ *for all compounds at both X- and Q-band frequencies. These spectra can be interpreted on the basis of a slightly distorted* D_{4h} *symmetry for* $S=5/2$*, with* $D = 0.05$-1.5 cm^{-1} *and* λ *(being equal to* E/D*)* $=0.01$-0.1*.*

The different values of the parameters for the several compounds can be explained by differences in the axial ligand-field strengths.

Introduction

Previous work[1] in the present series dealt with spectroscopic properties of Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II} in a ligand field of four pyrazoles and two anions with symmetry D_{4h}. It was also found that the corresponding manganese compounds $Mn(L)_4(A)_2$ were isomorphous with the above compounds.[2]

However, the electronic spectra of these manganese compounds did not yield information about the distortion from octahedral symmetry. The reasons for this are:

1. The ligand-field bands of high-spin Mn^{II} compounds are very weak;[3] (usually these compounds are colourless).

2. No clear band splittings with respect to octahedral Mn^{II} were observed[1] in the compounds $Mn(L)_4(A)_2$.

3. Theoretically additional ligand-field splittings—with respect to octahedral ones—are not expected to be large in tetragonal Mn^{II} compounds[4] even with considerable distortion.

Because of the fact that E.P.R. spectra of tetragonal Mn^{II} compounds are known to be rather different from the spectra of octahedral Mn^{II},[5,6] we investigated the E.P.R. spectra of these compounds. In recent years much progress has been made with the interpretation of these spectra.[6-10]

We investigated the E.P.R. spectra of solid compounds $Mn(L)_4(A)_2$ and Fe- or $Co((L)_4(A)_2$ containing 1-2% of Mn^{2+} ions, at both X- and Q-band frequencies. In this study L = pyrazole (Pz) and 3(5)-methylpyrazole (MPZ).

Experimental Section

Synthesis of the compounds. All compounds were synthesized as described previously[2,11] from the hydrated manganese(II) salts and the proper ligand ligand in ethanol. The Mn-doped Fe^{II} and Co^{II} compounds were prepared similarly, but with 1-2% Mn^{II} salt added.

E.P.R. Measurements. E.P.R. spectra were recorded with a Varian V-4502/3-10 A X- and Q-band spectrometer, equipped with a 12-inch Fieldial-regulated magnet and using 100 kHz field modulation frequency. X-band microwave frequencies were measured with a Hewlett-Packard 2590 A frequency converter and a Hewlett-Packard 5245 L electronic counter. Q-band frequencies were determined with a reference cavity in the Q-band microwave bridge. The magnetic field strength was measured with the Fieldial field regulator, which has been calibrated before with the aid of a Varian F-8A fluxmeter, coupled to the Hewlett Packard 5245 L electronic counter. All compounds were measured as powdered samples at room temperature.

Interpretation. The E.P.R. spectra of these manga-

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[*] Part IX. J. Reedijk, J.C.A. Windhorst, N.H.M. van Ham, and W.L. Groeneveld. *Rec. Trav. Chim.*, *91*, 234 (1971).

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Table I. Zero-field parameters for Manganese compounds, $Mn(L)_n(A)_2$

Parameters:	D					λ				
Anions:	NCS	NO_3	Cl	Br	I	NCS	NO_3	Cl	Br	I
Ligands										
Pyrazoles [a]	—	0.06	0.12	0.65	1.44	—	0.1	0.1	0.015	0.025
o-phenanthroline [b, c]	0.05	—	0.14	0.395	0.975	0.33	—	0.27	0.27	0.30
Pyridines [d]	0.03	—	0.16	0.54	0.87	0.0	—	0.1	0.01	0.01
biuret [b, c]	—	—	0.17	0.37	0.68	—	—	0.167	0.067	0.03

[a] This work; [b] bidentate ligand; [c] Ref. 12; [d] Ref. 6.

nese compounds can be described by a spin Hamiltonian of the form:

$$H = \beta H.g.S + S.D.S. + S.A.I. + \text{higher order zero-field terms}$$

In this study we have neglected the hyperfine interaction, since we were interested in the zero-field splitting, and have taken the centre of the six hyperfine peaks as the centre of the resonances. This is valid where the zero-field splitting is much greater than the hyperfine splitting which is true for the compounds under investigation. We have also neglected the higher order zero-field terms, since in other similar studies[5,6,10] these have been shown to be small. Transforming the remaining terms to one axis system, assuming tensor axes to be coincident, gives:

$$H = g.\beta.H.S. + D[S_z^2 - 1/3S(S+1)] + E(S_x^2 - S_y^2)$$

For ease of manupilation we have used $\lambda = E/D$ following Wickman.[12] The intensities were calculated by means of the formula:

$$I = \int_0^{\pi/2} <i|S_k|j>^2 d\theta$$

where:

S_k = the component of spin along the direction of the microwave magnetic field.

i and j are the wave functions of the involved levels.

For a fuller description of theory and calculations see reference 7.

Calculations methods. To obtain rough values for the parameters D and λ from the experimental spectra, the graphs published by Dowsing[7] and Aasa[8] were used. After that the parameters were refined by solving the complete spin Hamiltonian matrix by numeric methods. In all calculations frequencies of 9.520 GHz (X-band) and 34.000 GHz (Q-band) were used. These calculations were carried out at the IBM 360-50 computer at the University of Leyden.

Results

E.P.R. spectra were recorded at X-band frequencies (9.520±0.002 GHz) and Q-band frequencies (about 34.00±0.01 GHz) for the compounds of formula $Mn(L)_4(A)_2$ with L = pyrazole and (3(5)-methylpyrazole, and A = Cl^-, Br^-, I^-, and NO_3^-. For a few cases also dilutions in the corresponding isomorphous cobalt or iron compounds were investigated.

The spectra for the compounds with the same anion and either Pz or MPZ appeared to be very similar;

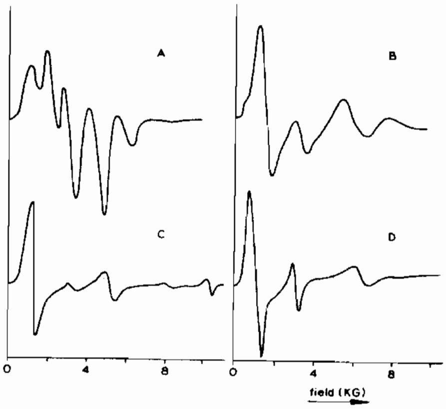

Figure 1. X.band spectra of tetragonal manganese compounds

A. $Mn(MPZ)_4(NO_3)_2$
B. $Mn(MPZ)_4Cl_2$
C. $Mn(MPZ)_4Br_2$
D. $Mn(MPZ)_4I_2$

Figure 2. Q-band spectra of tetragonal manganese compounds

A. $Mn(MPZ)_4(NO_3)_2$
B. $Mn(MPZ)_4Cl_2$
C. $Mn(MPZ)_4Br_2$
D. $Mn(MPZ)_4I_2$

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therefore the spectra will be discussed with varying anions. Figures 1-3 show a few spectra of some compounds illustrating band widths, band shapes and hyperfine splittings.

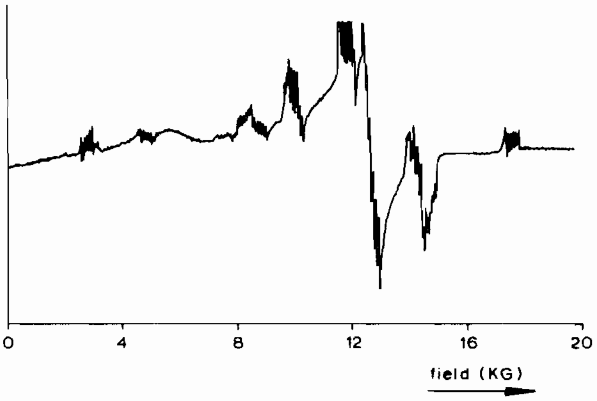

Figure 3. Q-band EPR spectrum of Mn^{2+} in $Fe(MPZ)_4Cl_2$.

The iodide compounds are characterized by the very strong absorption near $g_{eff}=6$ at both frequencies. The other absorptions have weaker intensities. The values found for the parameters are $D=1.44\pm0.03$ and $\lambda=0.025\pm0.010$.

For the bromides these values are $D=0.65\pm0.02$, $\lambda=0.015\pm0.010$. Because of the large number of bands in the spectra of the chlorides the parameters could be determined even more accurately, *viz.* $D=0.12\pm0.01$ and $\lambda=0.10\pm0.01$. The finite transition probability of some low-field absorptions indicates the presence of other terms in the spin Hamiltonian describing these compounds. It is most likely that the fourth order zero-field terms are not neglible in this situation.

Evidence for such fourth order zero-field splitting terms also comes from the results of the nitrate compounds. In these compounds many transitions that are expected to have zero transition probability, without the inclusion of fourth order terms, occur with positive intensity at low field. Unfortunately, the present calculation were unable to deduce the magnitude of these terms, although it is expected to be small. The value found for D is 0.06 ± 0.01; variation of λ in this range of D has little influence upon the spectra, so λ was found to be 0.10 ± 0.03.

To compare the magnitudes of the distortion parameters for the several anions and relative to other ligands in rather similar Mn^{II} compounds, Table I has been compiled. On considering this table we see that for our compounds, just as for the compounds containing the other ligands, the anion sequence with respect to increasing D-values is $NO_3^- < Cl^- < Br^- < I^-$. This sequence goes parallel with the spectrochemical series for these anions as studied for Cobalt(II) and Nickel(II).[13,14] Since pyrazoles are known to be rather strong ligands[2,11] we can explain these increasing D-values by an increasing difference between the axial and equatorial ligand-field strengthes in *trans*-octahedral molecular units. The rather small λ-values of our complexes also agree with this picture.[6]

However, when comparing the results of our pyrazoles with those of the pyridines, we see rather large differences in D, although it is known[15] that the ligand-field strengthes for the equatorial ligands are nearly equal. Thus on the basis of the same structural units (*trans*-octahedral MnN_4A_4) we would expect similar values for D in these compounds. The origin of the differences may be a strong hydrogen bond between the anion and the pyrazole ligands in these complexes.[16,17] This will weaken the metal-anion bond and yield larger values for D, just as found for the bromides and the iodides. The reverse, however, is observed for the chlorides, but in these compounds also λ is quite large and other effects may contribute to D. Comparison with the D values of the compounds containing the other two ligands (Table I) seems less useful, because of the fact that these are bidentate ligands, that are *cis*-coordinate (*o*-phenanthroline) or that are weaker ligands (biuret). For these latter ligands it is seen that the anion sequence holds, and in addition that the λ-values are quite large compared with our ligands.

From previous work[2] we known that the corresponding Fe, Co, and Ni compounds are isomorphous with the present Mn^{II} compounds. Since these latter compounds were studied by Mössbauer and electronic spectra, it seemed interesting to study a possible relationship between distortion parameters for Mn, Fe, Co, and Ni compounds. A list of the several parameters has been made in Table II.

We see from this table that especially for the halides, the D-value of the present study go parallel with the values for $Dq^{xy}-Dq^{z}$ and with $4Ds+5Dt$ (the e_g-electron splitting in a tetragonal ligand field). The position of the nitrate is somewhat uncertain; this may be due to a different crystal structure.

Although the Mössbauer quadrupole splitting is generally thought to be a rough measure of the distortion from cubic symmetry, in Table II we observe the reverse effect, *i.e.* the smallest ΔE_q for the iodides and the largest value for the nitrate. The reason for this may be that very large distortions, such as in our present compounds, produce a lattice asymmetry of about the same size as the t_{2g}-electron asymmetry[19] or possibly even larger. In that case the observed sequence is as would be expected.

Conclusions

Regarding the results discussed above, the following conclusions can be drawn:

1. The E.P.R. spectra of $Mn(pyrazole)_4(anion)_2$ can be explained on the basis of $S=5/2$ and *trans*-octahedral, D_{4h} symmetry.

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Table II. Comparison of distortion parameters for D_{4h} M(ligand))$_4$(A)$_2$

Parameters: [a]	D(cm^{-1})	Dq^{xy}—Dq^{z}(cm^{-1})			4Ds+5Dt(cm^{-1})			ΔE$_q$(mm/s)
Anion Metal ion:	Mn	Fe	Co	Ni	Fe	Co	Ni	Fe
NO_3^-	0.06	405	525	570	5000	5900	6500	2.81
Cl^-	0.12	330	370	410	4200	4500	4800	1.57
Br^-	0.65	490	510	535	6000	6100	6200	1.00
I^-	1.44	680	685	690	8200	7900	7600	0.56

[a] D = zero-field splitting (this work); Dq^{yx}—Dq^{z} = difference in crystalfield splitting for the equatorial and axial direction (ref. 18); 4Ds+5Dt= the e_g-electron splitting (ref. 18); ΔE$_q$ is the quadrupole splitting (ref. 19).

2. The distortion parameters D and λ agree with the spectrochemical positions of the anions. The D-values for the compounds with varying anions agree with other measures for the tetragonal distortion as obtained from electronic and Mössbauer spectra for the Ni, Co, and Fe compounds.

3. Compared with the corresponding pyridine compounds, the D-values for the pyrazole compounds are higher due to hydrogen bonding between the anions and the pyrazole ligands.

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