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An ESR Study of Manganese(II) Ions in Complexes of Diacetamide

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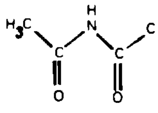
Abstract

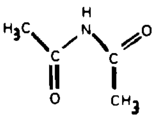
ESR spectra at both X- and Q-band are reported for Mn(II) ions doped at a nominal 1% in the lattices of $[M(DA)_2(H_2O)_2]X_2$ (M = Mg, Co and Ni; X = Cl or Br), $[Mg(DA)_2(H_2O)_2](NO_3)_2$, $[Co(DA)_4(H_2O)_2]Br_2$, $M(DA)_2Cl_2$ (M = Mg, Co and Ni) and $M(DA)_2(NO_3)_2$ (M = Co and Zn). The zero-field splitting parameters D and λ (= E/D) are deduced. The observed values of D and λ for all the hydrated complexes are consistent with an MO_6^{2+} chromophore, suggesting the coordination of water molecules. Higher values of D are observed for $M(DA)_2Cl_2$ (M = Mg, Co and Ni) than for the hydrated analogues. The positive sign of D, deduced for the first time from the hyperfine spacing at Q-band, suggests the *trans*-coordination of chloride ions and very high λ values indicate considerable in-plane distortion.

Introduction

Solid diacetamide (DA) has been found to exist both in *cis* (A) and in *trans* (B) configurations [1]. However, due to the pronounced tendency of the *trans* form to dimerize, the most stable form of the free ligand is the dimeric compound (C) [2]. The *cis* form is unstable and reverts to the *trans* form on standing, but when it acts as a ligand, diacetamide forms stable complexes in either of these two configurations.



A



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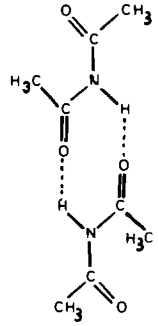

C

A large number of complexes, formed by diacetamide with metal(II) halides and nitrates have been reported previously, but physical studies have been limited to their infrared and visible spectra [2–4]. It has been suggested from the infrared data [3, 4] that the diacetamide molecules in most of the complexes studied here are in the *cis* form (A) and acting as bidentate ligands, coordinating through both of their carbonyl oxygen atoms. Only in the compound $[Co(DA)_4(H_2O)_2]Br_2$ has monodentate coordination of the ligand been suggested. Recently, the X-ray crystal structure of $[Co(DA)_2(H_2O)_2]Cl_2$ has been studied, and shows the ligand molecules to be *cis*-bidentate, with the water molecules occupying the *trans* positions [5].

We report here an ESR study of manganese(II) ions doped into the complexes of diacetamide with divalent metal(II) halides and nitrates, which confirms that in all the hydrated complexes water molecules are coordinated at *trans* positions and also permits a measurement of the zero-field splitting parameters D and λ (= E/D).

Experimental

Preparation of Complexes

All of the complexes were prepared by previously reported methods [3, 4] and had good analyses.

The nominal doping level was 1% in all cases.

X-band spectra were obtained using a Varian E12 spectrometer. Q-band spectra were obtained with a Bruker ER200D-SRC spectrometer and an ER 078 15-inch electromagnet. All samples were measured as polycrystalline solids.

Results and Discussion

ESR spectra have been obtained at both X- and Q-band frequencies for 1% of manganese(II) ions doped into the lattices of complexes $[M(DA)_2$-

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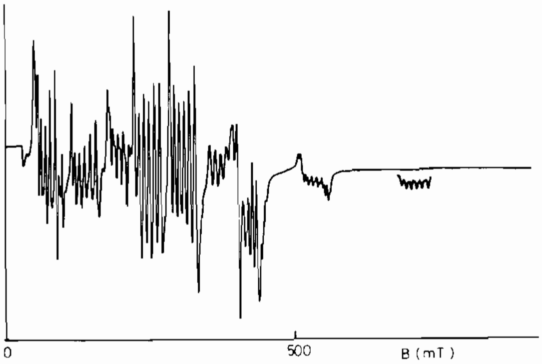

Fig. 1. X-band ESR spectrum of $[Co(Mn)(DA)_2(H_2O)_2]Cl_2$.

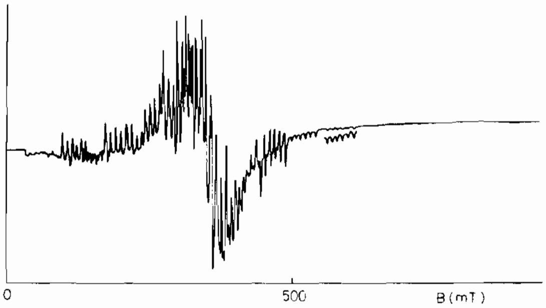

Fig. 2. X-band ESR spectrum of $Zn(Mn)(DA)_2(NO_3)_2$.

$(H_2O)_2]X_2$ (M = Mg, Co and Ni; X = Cl or Br), $[Mg(DA)_2(H_2O)_2](NO_3)_2$, $[Co(DA)_4(H_2O)_2]Br_2$, $M(DA)_2Cl_2$ (M = Mg, Co and Ni) and $M(DA)_2(NO_3)_2$ (M = Co and Zn).

At X-band frequency, all of these complexes gave good quality but very complicated spectra (Fig. 1), with considerable overlapping of transitions and detailed interpretation was difficult. The spectra of the complexes $[M(DA)_2(H_2O)_2]X_2$ (M = Mg, Co and Ni; X = Cl or Br), $[Co(DA)_4(H_2O)_2]Br_2$ and $[Mg(DA)_2(H_2O)_2](NO_3)_2$ are of the same general type and suggest that all of these complexes have similar structures. The highest bands observed in the 640–740 mT region, for most of these hydrated complexes, suggested D values of about 0.07–0.10 cm^{-1} for them.

The X-band spectra for $M(DA)_2Cl_2$ (M = Mg, Co and Ni) are very similar to one another but entirely different from those of the analogous hydrated complexes. The strong absorption observed near zero field suggested D values of about 0.1–0.2 cm^{-1}.

In the X-band spectra of complexes $M(DA)_2(NO_3)_2$ (M = Co and Zn), the strongest bands occurred in the $g_{eff} = 2$ region (Fig. 2), indicating much lower D values. The highest band observed around 590 mT suggested a D value of about 0.06 cm^{-1}.

The Q-band spectra of all of these complexes were much better resolved (Fig. 3) and therefore, were used to determine the precise values of D and λ (= E/D), for the individual compounds, in the spin Hamiltonian (1). Experimental resonance fields agreed very well with those calculated, using

$$\mathcal{H} = g\beta BS + D(S_z^2 - 35/12) + E(S_x^2 - S_y^2) \qquad (1)$$

the program ESRS [6], by exact diagonalization of the matrix derived from eqn. (1) with $g_{iso} = 2.00$. Details are given in Tables 1–3.

The positions of the off-axis transitions were calculated for the Q-band spectra of many of these complexes and fitted very well with the weak bands

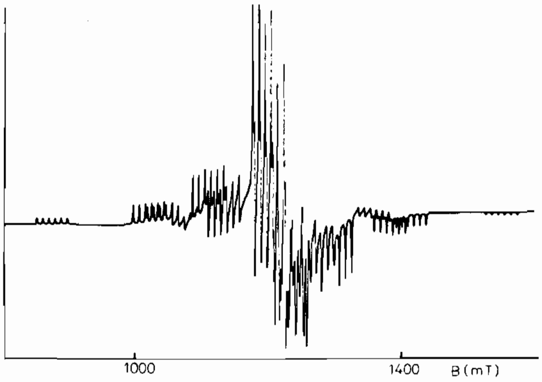

Fig. 3. Q-band ESR spectrum of $[Mg(Mn)(DA)_2(H_2O)_2]Br_2$.

TABLE 1. Q-band ESR spectrum (mT) of $[Ni(Mn)(DA)_2(H_2O)_2]Cl_2$

Observed (ν = 33.870 GHz)	Calculated for $D = 0.088\ cm^{-1}$, $\lambda = 0.010$			
	B	*TP*	Field direction	Levels
429.6w/m	428.6	0.04	$\theta = 30°, \phi = 00°$	5- -2
	430.2	0.05	$\theta = 31°, \phi = 90°$	5- -2
Region	636.0	0.24	$\theta = 66°, \phi = 00°$	4- -2
616–666w	640.2	0.24	$\theta = 66°, \phi = 90°$	4- -2
Overlap	702.1	0.13	$\theta = 14°, \phi = 00°$	5- -3
680–728w	702.6	0.15	$\theta = 15°, \phi = 90°$	5- -3
823.6w/m	831.7	5.02	*z*	2- -1
1023.5m/s	1020.8	8.02	*z*	3- -2
	1024.0	4.25	*y*	6- -5
1038.8m	1035.6	4.24	*x*	6- -5
1106.8s	1105.8	7.29	*y*	5- -4
1109.9m/s	1110.5	7.28	*x*	5- -4
1195.0s	1195.0	8.84	*x*	4- -3
	1195.6	8.83	*y*	4- -3
Region s	1209.9	9.00	*z*	4- -3
1289.9s	1290.6	8.52	*x*	3- -2
1296.2s/m	1296.7	8.50	*y*	3- -2
1400.0s/m	1399.0	7.99	*z*	5- -4
	1399.4	5.80	*x*	2- -1
1410.8m	1410.5	5.78	*y*	2- -1
1588.1w	1588.2	4.99	*z*	6- -5

TABLE 2. Q-band ESR spectrum (mT) of $Mg(Mn)(DA)_2Cl_2$

Observed (ν = 33.865 GHz)	Calculated for D = 0.149 cm^{-1}, λ = 0.180			
	B	*TP*	Field direction	Levels
Region 225–282w	248.0	0.01	$\theta = 90°, \phi = 67°$	6- -3
	248.9	0.10	$\theta = 79°, \phi = 90°$	6- -3
Region 446–530w	411.7	0.05	$\theta = 09°, \phi = 00°$	5- -2
	479.2	0.13	$\theta = 13°, \phi = 90°$	5- -2
577.2w	577.6	5.56	z	2- -1
	600.6	0.84	$\theta = 55°, \phi = 90°$	4- -2
743.4w	742.8	3.92	y	6- -5
	751.1	0.79	$\theta = 65°, \phi = 90°$	4- -2
891.7m/s	890.6	8.56	z	3- -2
958.9m	957.8	6.84	y	5- -4
1094.3w	1095.2	3.62	x	6- -5
1104.9m	1104.3	6.63	x	5- -4
1150.5s	1151.5	8.62	x	4- -3
1185.0s	1184.6	8.50	y	4- -3
Region s	1205.3	9.20	z	4- -3
	1240.5	8.95	x	3- -2
1380.2w	1380.2	6.64	x	2- -1
1430.3s	1430.8	8.48	y	3- -2
1524.0m/s	1523.9	7.78	z	5- -4
1710.6w/m	1709.4	6.04	y	2- -1
1850.5w	1849.4	4.59	z	6- -5

TABLE 3. Q-band ESR sepectrum (mT) of $Co(Mn)(DA)_2(NO_3)_2$

Observed (ν = 33.865 GHz)	Calculated for D = 0.059 cm^{-1}, λ = 0.130			
	B	*TP*	Field direction	Levels
958.8w	957.7	5.14	z	2- -1
1037.3w/m	1037.5	4.55	y	6- -5
1083.4m	1083.5	8.13	z	3- -2
1120.6m	1119.7	7.59	y	5- -4
	1137.6	4.43	x	6- -5
1165.0m	1166.7	7.50	x	5- -4
1201.0m	1201.7	8.93	x	4- -3
1205.7s	1205.2	8.92	y	4- -3
1209.9s	1209.7	9.02	z	4- -3
1245.3m	1243.0	8.43	x	3- -2
1293.8m/s	1291.0	5.60	x	2- -1
	1294.3	8.31	y	3- -2
1337.4m	1336.1	7.91	z	5- -4
1388.4w/m	1387.8	5.45	y	2- -1
1463.0w	1463.0	4.87	z	6- -5

observed at low field. However, two weak bands observed around 300 and 367 mT, in the spectrum of $[Mg(DA)_2(H_2O)_2]Cl_2$, could not be fitted with any of the calculated off-axis transitions within the principal planes.

Previously, the sign of the parameter D has been determined from the variations in the mean spacing of the hyperfine components of the extreme z-axis transitions, at X-band frequency [7, 8]. This means that the full range of the spectrum, at X-band frequency, has to be observed, and the maximum value of $[D]$ for which this method is practicable is about 0.07 cm^{-1}.

For the first time, the variation in the average hyperfine spacing of the sextets has been observed at Q-band frequency, which made it possible to determine the sign of D for these complexes, with D values higher than 0.07 cm^{-1}. As at X-band, the effect was greatest for the extreme z-axis transitions, but at Q-band these are observed for $[D]$ up to about 0.20 cm^{-1}.

For all the halide complexes, in the Q-band spectra, this spacing was greater for the highest field observed band than for the lowest field allowed transition. For example, for $Co(Mn)(DA)_2Cl_2$ the average spacing on the band at 577.2 mT was 8.7 mT, compared with 9.1 mT on the band at 1850.5 mT, suggesting that D must be positive (Fig. 4).

The values of D and λ for these complexes are listed in Table 4. For all the hydrated complexes of metal halides and nitrates the values of D and λ are very similar to one another, but considerably different from the anhydrous analogues. These ESR results therefore suggest that, like $[Co(DA)_2(H_2O)_2]Cl_2$ [5], all of these complexes contain a MO_6^{2+} chromophore, with two chelating diacetamides and water molecules in the *trans* positions.

The positive sign of D observed for these hydrates indicates that the in-plane ligand field is stronger than that on the z-axis. This is despite the fact that in the X-ray crystal structure of $[Co(DA)_2(H_2O)_2]Cl_2$ [5], the bonds between cobalt and the oxygen atoms of the diacetamide are longer (2.078 and 2.085 Å) than those with water (2.044 Å). This may mean that the major D-tensor axis does not lie along the metal ion–water bonds. However, diacetamide normally exerts a stronger ligand field than water (Dq = 900 cm^{-1} compared with 850 cm^{-1} for water) [9] and in $[Co(DA)_2(H_2O)_2]Cl_2$ the water molecules are strongly hydrogen bonded. This would leave a

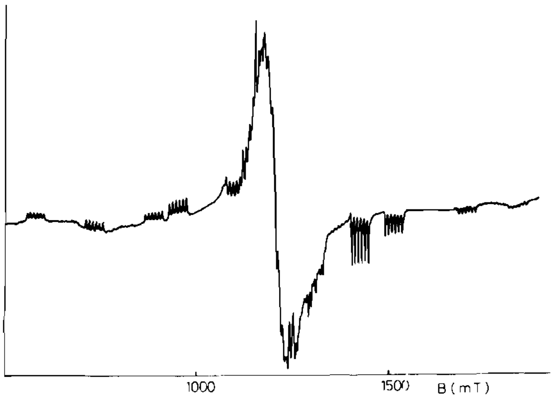

Fig. 4. Q-band ESR spectrum of $Co(Mn)(DA)_2Cl_2$.

TABLE 4. ZFS parameters of Mn(II) in metal halides and nitrates complexes

Complex	D (cm^{-1})	λ
$[Mg(DA)_2(H_2O)_2]Cl_2$	0.091	0.010
$[Co(DA)_2(H_2O)_2]Cl_2$	+0.091	0.003
$[Ni(DA)_2(H_2O)_2]Cl_2$	+0.088	0.010
$[Mg(DA)_2(H_2O)_2]Br_2$	+0.079	0.053
$[Co(DA)_2(H_2O)_2]Br_2$	0.085	0.030
$[Co(DA)_4(H_2O)_2]Br_2$	+0.098	0.035
$[Ni(DA)_2(H_2O)_2]Br_2$	+0.077	0.065
$[Mg(DA)_2(H_2O)_2](NO_3)_2$	0.080	0.060
$Mg(DA)_2Cl_2$	+0.149	0.180
$Co(DA)_2Cl_2$	0.148	0.189
$Ni(DA)_2Cl_2$	0.151	0.180
$Co(DA)_2(NO_3)_2$	0.059	0.130
$Zn(DA)_2(NO_3)_2$	0.058	0.135

considerable negative charge on the oxygen of the water, making it a stronger π-donor, and thus further weakening its crystal field effect. In this connection it may be significant that for each metal ion the D value is greater for the chloride than for the bromide.

The very similar values of D and λ, found for $M(DA)_2Cl_2$ (M = Mg, Co and Ni) suggest the presence of an identical chromophore. The positive sign of D indicates *trans*-coordination of Cl^- ions, and the higher values of D observed for these complexes than for the analogous hydrated complexes are in line with the lower ligand field strength of chlorides than the water molecules. For all these complexes the λ values are very high indicating considerable in-plane distortion and the approximate symmetry of these complexes should perhaps be described as D_{2h} rather than D_{4h}. This observation could be explained by a tendency for the in-plane structure to twist towards tetrahedral as the axial field is reduced.

The D and λ values observed for $M(DA)_2(NO_3)_2$ (M = Co and Zn) are rather similar indicating an essentially identical structure. The zinc complex has been studied previously [2] and on the basis of infrared, NMR and conductance data, the nitrate ions have been reported to be coordinated with the central metal ions and six coordination was suggested for this complex. The lower values of D observed here are consistent with this observation and confirm the likelihood of a MO_6 chromophore. The nitrate ions apparently produce a slightly stronger crystal field effect than do water molecules in this type of complex.

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References

1 T. Uno and K. Machida, *Bull. Chem. Soc. Jpn., 34* (1961) 545.

2 P. S. Gentile, T. A. Shankoff and J. Carlotto, *J. Inorg. Nucl. Chem., 28* (1966) 979.

3 P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem., 28* (1966) 1283.

4 P. S. Gentile and T. A. Shankoff, *J. Inorg. Nucl. Chem., 27* (1965) 2301.

5 T. S. Khodashova, V. P. Nikolaev, M. A. Porai-Koshits, L. A. Butman and E. I. Tabize, *Koord. Khim., 12* (1986) 128.

6 D. Vivian and J. F. Gibson, *J. Chem. Soc., Faraday Trans. II*, (1975) 1640.

7 R. B. Birdy and M. Goodgame, *J. Chem. Soc., Dalton Trans.*, (1977) 461.

8 M. Goodgame and J. N. Okey, *J. Chem. Soc., Dalton Trans.*, (1985) 75.

9 C. S. Kraihanzel and S. C. Grenda, *Inorg. Chem., 4* (1965) 1037.