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Preparation and spectroscopic studies of the complexes of diacetamide with metal(II) perchlorates ☆

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Abstract

The preparations of complexes formed by diacetamide (DA) with metal(II) perchlorates in 1:4 and 1:2 stoichiometry are reported. The ESR spectra, at both X- and Q-band, of Mn(II) ions doped in all these complexes and also those of 1:3 stoichiometry are reported, and the zero-field splitting parameters D and $\lambda(=E/D)$ are deduced. Very small values of D observed for complexes $M(DA)_3(ClO_4)_2$ (M = Fe, Co, Ni) are consistent with an MO_6^{2+} chromophore. The corresponding Zn and Cd complexes have distinctly higher D values. The identical values of D and λ, observed for all complexes with 1:4 stoichiometry, suggest identical structures and the X-ray powder patterns of these complexes also show marked resemblances. Considerably higher values of λ for $M[(DA)_2(H_2O)_2](ClO_4)_2$ (M = Co, Zn) show appreciable distortion. IR spectra distinguish coordinated from hydrogen bonded diacetamide.

Keywords: Alkali earth complexes; Transition metal complexes; Diacetamide complexes

1. Introduction

The complexes of diacetamide with metal(II) perchlorates in 1:3 stoichiometry have been prepared and their IR spectra, visible spectra and conductivity measurements have already been reported [1], but those of 1:4 and 1:2 ratio have received very little attention. The exception is the magnesium perchlorate complex of 1:4 stoichiometry for which the X-ray crystal structure has been reported [2]. Each metal ion is coordinated with two diacetamide molecules, acting as bidentate ligands [3], and the *trans* positions are occupied by water molecules. The remaining two diacetamide molecules are hydrogen bonded and are not involved in coordination.

Here, we report the preparation of a series of complexes formed by diacetamide with metal perchlorates in 1:4 and 1:2 stoichiometry. The ESR spectra of Mn(II) ions doped into the lattices of these complexes and also those with 1:3 stoichiometry have been obtained in order to study their structures. X-ray powder patterns and IR spectra have been used to confirm the structures of the metal perchlorate complexes of 1:4 stoichiometry.

2. Experimental

2.1. Preparation of complexes

All the chemicals were of reagent grade and were used without further purification.

2.1.1. $[Mg(DA)_2(H_2O)_2](ClO_4)_2\cdot 2DA$

This complex was prepared by the previously reported method [2]. *Anal.* Found: C, 29.09; H, 4.82; N, 8.71. Calc. for $[Mg(DA)_2(H_2O)_2](ClO_4)_2\cdot 2DA$: C, 28.95; H, 4.82; N, 8.44%.

2.1.2. $[M(DA)_2(H_2O)_2](ClO_4)_2\cdot 2DA$ (M = Fe, Co, Ni, Zn)

All of these complexes were prepared by grinding thoroughly the mixtures of the corresponding hydrated metal(II) perchlorates and diacetamide in the ratio of 1:5. The product thus formed was washed with diethyl ether to remove the excess of ligand and dried in vacuo for 10 min.

☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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The complexes of Fe, Co and Ni can also be prepared by mixing a hot solution of metal perchlorate hexahydrate (0.01 mol) in ethyl acetate (30 cm^3) with a solution of diacetamide (0.05 mol) in ethyl acetate (30 cm^3). The precipitate thus formed was filtered off, washed with diethyl ether and dried in vacuo for 30 min. *Anal.* Calc. for $[Fe(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$: C, 27.63; H, 4.61; N, 8.06. Found: C, 27.43; H, 4.76; N, 7.92%. Calc. for $[Co(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$: C, 27.63; H, 4.61; N, 8.06. Found: C, 27.17; H, 4.52; N, 7.77%. Calc. for $[Co(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$: C, 27.51; H, 4.59; N, 8.02. Found: C, 27.17; H, 4.51; N, 7.7%. Calc. for $[Zn(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$: C, 27.25; H, 4.54; N, 7.95. Found: C, 26.86; H, 4.45; N, 7.92%.

2.1.3. $M(DA)_3(ClO_4)_2$ (M = Mg, Fe, Co, Ni)

These complexes were prepared by drying the corresponding 1:4 complexes in vacuo for 24 h. *Anal.* Calc. for $Mg(DA)_3(ClO_4)_2$: C, 27.38; H, 4.00; N, 7.98. Found: C, 27.29; H, 4.70; N, 8.14%. Calc. for $Fe(DA)_3(ClO_4)_2$: C, 25.82; H, 3.76; N, 7.53. Found: C, 25.77; H, 3.79; N, 7.58%. Calc. for $Co(DA)_3(ClO_4)_2$: C, 25.67; H, 3.74; N, 7.49. Found: C, 25.15; H, 5.39; N, 7.25%. Calc. for $Ni(DA)_3(ClO_4)_2$: C, 25.68; H, 3.75; N, 7.49. Found: C, 25.58; H, 3.71; N, 7.09%.

2.1.4. $M(DA)_3(ClO_4)_2$ (M = Zn, Cd)

A hot solution of metal perchlorate hexahydrate (0.01 mol) in ethyl acetate (25 cm^3) was mixed with a hot solution of diacetamide (0.04 mol) in ethyl acetate (25 cm^3). The white precipitates thus formed were filtered off, washed with diethyl ether and dried in vacuo for 4 h. *Anal.* Calc. for $Zn(DA)_3(ClO_4)_2$: C, 25.38; H, 3.70; N, 7.40. Found: C, 25.17; H, 4.15; N, 7.37%. Calc. for $Cd(DA)_3(ClO_4)_2$: C, 23.44; H, 3.42; N, 6.84. Found: C, 23.35; H, 3.36; N, 6.84%.

2.1.5. $[M(DA)_2(H_2O)_2](ClO_4)_2$ (M = Co, Zn)

Both complexes were prepared by a similar method to that used for $Zn(DA)_3(ClO)_2$, but the metal to ligand ratio used was 1:2. *Anal.* Calc. for $[Co(DA)_2(H_2O)_2](ClO_4)_2$: C, 19.36; H, 3.62; N, 5.64. Found: C, 19.14; H, 3.39; N, 5.46%. Calc. for $[Zn(DA)_2(H_2O)_2](ClO_4)_2$: C, 19.11; H, 3.58; N, 5.57. Found: C, 19.62; H, 3.42; N, 5.69%.

Analytical results were obtained by the Imperial College Micro-analytical Laboratory.

X-band ESR spectra were obtained using a Varian E12 spectrometer. Q-band spectra were obtained with a Bruker ER 200D-SCR spectrometer and an ER 078 15-inch electromagnet. All samples had a nominal doping of 1% and were measured as polycrystalline solids.

X-ray powder data was collected using a Siemens D500 diffractometer.

IR spectra were obtained using a Perkin-Elmer 1720 FTIR spectrometer.

3. Results and discussion

3.1. Electron spin resonance spectra

ESR spectra were measured at both X-band and Q-band for the 1% of manganese(II) ions doped into the lattices of compounds $M(DA)_3(ClO_4)_2$ (M = Mg, Fe, Co, Zn, Cd), $M(DA)_4(H_2O)_2(ClO_4)_2$ (M = Mg, Fe, Co, Ni, Zn) and $[M(DA)_2(H_2O)_2](ClO_4)_2$ (M = Co, Zn).

At X-band, the spectra of complexes $M(DA)_3(ClO_4)_2$ (M = Mg, Fe, Co) are very similar to one another. The strongest bands appeared in the $g_{eff} = 2$ region, suggesting very low values of D for these compounds. By contrast, in the X-band spectra of the apparently analogous zinc and cadmium complexes, considerable overlapping of transitions was seen over a wide range of magnetic field (Fig. 1) and the highest band observed around 800 mT, in the spectra of both of these complexes, suggested D values of 0.11–0.12 cm^{-1}.

The better resolved Q-band spectra (Fig. 2) were used to calculate the zero-field splitting parameters D

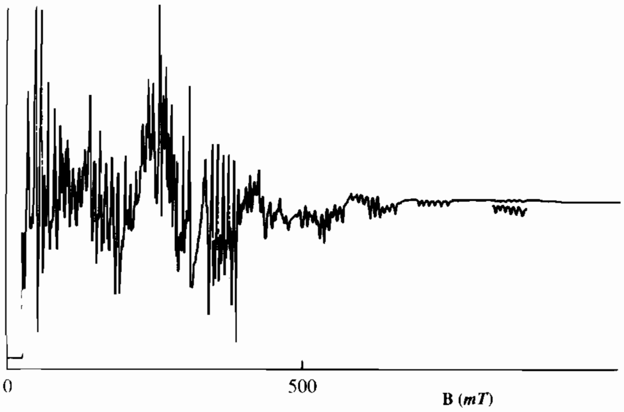

Fig. 1. X-band ESR spectrum of $Cd(Mn)(DA)_3(ClO_4)_2$.

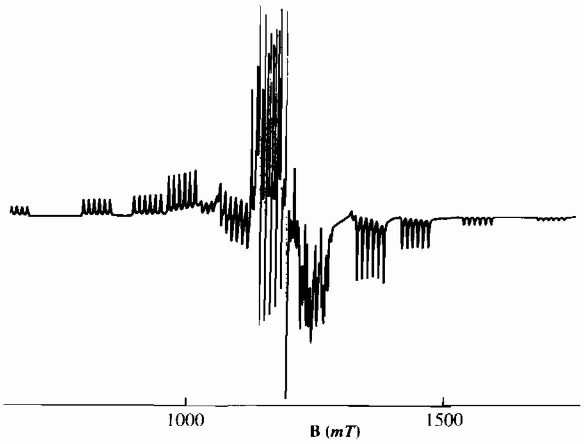

Fig. 2. Q-band ESR spectrum of $Cd(Mn)(DA)_3(ClO_4)_2$.

and λ ($=E/D$), for all of these complexes in the spin Hamiltonian (1).

$$\mathscr{H} = g\beta BS + D(S_{z^2} - 1/3S(S+1)) + E(S_{x^2} - S_{y^2}) \qquad (1)$$

The observed resonance fields fitted very well with those calculated, using the program ESRS [4], by exact diagonalization of the matrix derived from (1) with $g_{iso} = 2.00$ (Table 1). Additionally, at Q-band frequency, a difference was observed between the mean hyperfine spacing of the sextets for the extreme z-axis transitions, for these zinc and cadmium complexes. The spacing was greater on the lowest field than on the highest field transition, so assuming that the hyperfine coupling constant A is negative, D must also be negative [5].

Values of D and λ ($=E/D$) are listed in Table 2. For the complexes $M(Mn)(DA)_3(ClO_4)_2$ (M = Fe, Co, Ni), the observed values of D are very similar to one another. The small values indicate a symmetry very close to O_h for the MO_6^{2+} chromophore.

In contrast, the D and λ values observed for the Zn and Cd analogues are distinctly higher showing considerable distortion from cubic symmetry. They are rather similar [6] to the values observed for the histidine complexes of Zn and Cd. The X-ray crystal structures for these histidine complexes have been reported previously and the metal ions were found to be coordinated tetrahedrally with four nitrogens and very loosely associated with two oxygen atoms [7,8]. It seems possible that the complexes $M(DA)_3(ClO_4)_2$ (M = Zn and Cd), also have a basic tetrahedral structure, but with the remaining oxygen atoms loosely attached to the central metal ions.

Table 1
Q-band ESR spectrum (mT) of $Zn(Mn)(DA)_3(ClO_4)_2$

Observed ($v = 33.860$ GHz)	Calculated for $D = -0.1165$ cm^{-1}, $\lambda = 0.125$			
	B	TP [a]	Field direction	Levels
263.6w				
453.4w				
519.1w				
712.4w	712.0	5.29	z	6–5
880.1w	880.8	4.11	y	2–1
961.0m	959.7	8.28	z	5–4
1030.7m	1030.7	7.10	y	3–2
	1072.3	3.92	x	2–1
1116.7m	1114.2	6.96	x	3–2
1177.5s	1177.2	8.75	x	4–3
1190.2s	1190.8	8.70	y	4–3
1208.7s	1208.7	9.09	z	4–3
Region	1264.0	8.74	x	5–4
1366.3m	1365.2	8.49	y	5–4
1380.2w	1378.8	6.20	x	6–5
1457.4m/w	1457.7	7.86	z	3–2
1559.9w	1559.3	5.89	y	6–5
1709.8w	1709.1	4.77	z	2–1

[a] TP = transition probability.

Table 2
ZFS parameters of Mn(II) in metal perchlorate complexes

Complex	D (cm^{-1})	λ
$[Mg(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	+0.0810	0.078
$[Fe(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	+0.0805	0.080
$[Co(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	+0.0810	0.080
$[Ni(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	0.0790	0.090
$[Zn(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	+0.0805	0.082
$Mg(DA)_3(ClO_4)_2$	0.0190	0.070
$Fe(DA)_3(ClO_4)_2$	0.0205	[a]
$Co(DA)_3(ClO_4)_2$	0.0200	0.090
$Zn(DA)_3(ClO_4)_2$	−0.1165	0.125
$Cd(DA)_3(ClO_4)_2$	−0.1107	0.146
$[Co(DA)_2(H_2O)_2](ClO_4)_2$	0.0520	0.200
$[Zn(DA)_2(H_2O)_2](ClO_4)_2$	0.0525	0.200

[a] Not determined.

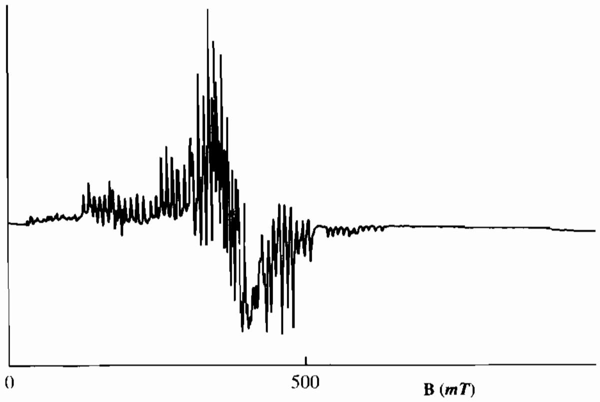

Fig. 3. X-band ESR spectrum of $[Ni(Mn)(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$.

An alternative possibility that these compounds have a distorted trigonal-prismatic coordination seems less likely. Although the D values are similar to those found [9] for $K[Cd(Mn)(acac)_3] \cdot H_2O$, which has a trigonal-prismatic structure [10], the λ values are very different. Moreover, this structure would require all the C=O groups to be equivalent, which is not supported by the IR data (vide infra).

At X-band frequency, all the complexes $M(Mn)(DA)_4(H_2O)_2(ClO_4)_2$ (M = Mg, Fe, Co, Ni, Zn) gave good quality but very complicated spectra (Fig. 3), with considerable overlapping of transitions, and detailed interpretation was difficult. However, the highest bands observed in the 620–720 mT region, for most of these complexes, suggested D values of 0.07–0.10 cm^{-1}. The Q-band spectra were very well resolved and gave the values of D and λ very easily (Table 3).

Again the sign of D for these complexes was obtained from the variations in the average hyperfine spacing of the extreme z-axis transitions at Q-band frequency. Except for the nickel complex, where the quality of the spectrum was not good enough to measure the small differences involved, this spacing was greater for

Table 3
Q-band ESR spectrum (mT) of $[Fe(Mn)(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$

Observed ($v = 33.875$ GHz)	Calculated for $D = 0.0805$ cm^{-1}, $\lambda = 0.080$			
	B	*TP*	Field direction	Levels
430.5w	421.2	0.02	$\theta = 31°$, $\phi = 00°$	5–2
	429.8	0.05	$\theta = 35°$, $\phi = 90°$	5–2
594–674w	622.5	0.17	$\theta = 67°$, $\phi = 00°$	4–2
	644.9	0.19	$\theta = 68°$, $\phi = 90°$	4–2
865.1w	865.5	5.12	*z*	2–1
1002.1w	1002.8	4.35	*y*	6–5
1038.1m	1037.6	8.11	*z*	3–2
1087.6w/m	1087.2	4.26	*x*	6–5
1098.7m	1098.2	7.39	*y*	5–4
1135.4m/s	1136.7	7.32	*x*	5–4
1196.1m/s	1195.8	8.87	*x*	4–3
1199.9s	1199.9	8.86	*y*	4–3
1209.3s	1209.8	9.03	*z*	4–3
1267.8s/m	1265.5	8.53	*x*	3–2
1308.4m	1309.4	8.42	*y*	3–2
	1347.2	5.79	*x*	2–1
1383.7m/w	1382.3	7.93	*z*	5–4
1429.7w	1428.0	5.65	*y*	2–1
1556.4w	1555.0	4.89	*z*	6–5

the highest-field observed band than for the lowest-field allowed transition, and hence *D* is positive.

The values of *D* and λ of these 1:4 complexes (Table 2) are very similar to one another and are consistent with some distortion of an MO_6^{2+} chromophore. This result is in line with the crystal structure reported for the magnesium perchlorate complex [2]. It is likely that all of these compounds have similar structures, and like the Mg complex should correctly be formulated as $[M(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$.

The positive sign of *D* observed in this case suggests that the ligand field is stronger on the *x*- and *y*-axes than on the *z*-axis, despite the fact that in the X-ray crystal structure of $[Mg(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$ the observed bond lengths between the magnesium and oxygen atoms of diacetamide (2.041 and 2.048 Å) are greater than between the magnesium and water (2.026 Å). This may mean that the principal *D*-tensor axis does not lie along the metal–water bonds. However, the reported *Dq* value of diacetamide (900 cm^{-1}) is higher than that of water (850 cm^{-1}) [1]. Also in $[Mg(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$ the water molecules are strongly hydrogen bonded, which would further weaken their crystal field effect.

The ESR spectra of the complexes $[M(DA)_2(H_2O)_2](ClO_4)_2$ (M = Co, Zn) are similar to one another. The X-band spectra were of very good quality, with strong transitions in the $g_{eff} = 2$ region (Fig. 4). The highest band observed around 560 mT suggests *D* values of about 0.05 cm^{-1}. The well resolved Q-band spectra (Table 4) gave the values of $D = 0.052$ cm^{-1} and $\lambda = 0.200$.

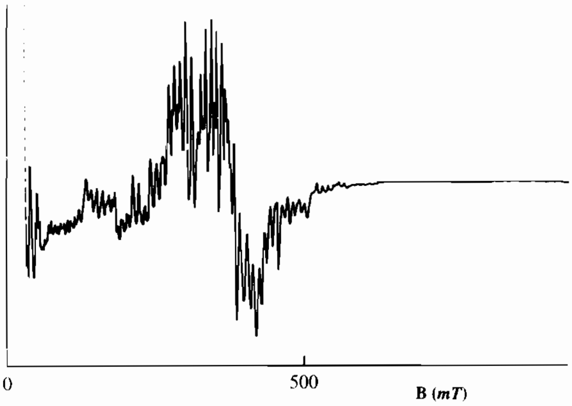

Fig. 4. X-band ESR spectrum of $[Zn(Mn)(DA)_2(H_2O)_2](ClO_4)_2$.

Table 4
Q-band ESR spectrum (mT) of $[Co(Mn)(DA)_2(H_2O)_2](ClO_4)_2$

Observed ($v = 33.865$ GHz)	Calculated for $D = 0.0520$ cm^{-1}, $\lambda = 0.200$			
	B	*TP*	Field direction	Levels
985.4w	985.4	5.20	*z*	2–1
1031.0w/m	1031.9	4.63	*y*	6–5
1097.9m	1096.9	8.17	*z*	3–2
1119.3m	1118.1	7.66	*y*	5–4
1169.5w	1168.7	4.46	*x*	6–5
	1182.7	7.53	*x*	5–4
1202.3s	1202.2	8.95	*x*	4–3
1206.7s	1206.4	8.94	*y*	4–3
1209.4s	1208.9	9.03	*z*	4–3
1227.0s	1227.3	8.42	*x*	3–2
	1258.3	5.57	*x*	2–1
1296.4s/m	1297.3	8.25	*y*	3–2
1320.3m	1321.6	7.87	*z*	5–4
1392.3w	1391.0	5.37	*y*	2–1
1435.3w	1435.0	4.82	*z*	6–5

The identical values of *D* and λ for these two complexes indicate similar structures. The small value of *D* corresponds with a chromophore of symmetry fairly close to cubic, but the rather high value of λ suggests either a tetrahedron of ligands or rhombic distortion of an octahedron. Probably, as in the tris-complexes of Zn and Cd, in these complexes the diacetamide molecules are unsymmetrically coordinated, with one oxygen atom of each only loosely attached to the central metal. This result again corresponds with the IR spectra (Table 5), where a second band appeared in the carbonyl stretching region. Such an arrangement would give effectively rhombic symmetry, and lead to the observed high λ values.

3.2. X-ray powder diffraction patterns

In view of the similarity in the ESR spectra of $M(Mn)(DA)_4(H_2O)_2(ClO_4)_2$ their X-ray powder dif-

Table 5
Characteristic IR spectral bands of metal perchlorate complexes

Compound	C=O stretching bands		Imide III bands	
$[Mg(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	1756s	1742s	1247s	1224s
$[Fe(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	1756s	1721s	1251s	1225s
$[Co(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	1755s	1729s	1243s	1225s
$[Ni(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	1756s	1727s	1248s	1226s
$[Zn(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$	1754s	1728s	1251s	1224s
$Mg(DA)_3(ClO_4)_2$	1735vs		1254s	
$Fe(DA)_3(ClO_4)_2$	1721vs		1255s	
$Co(DA)_3(ClO_4)_2$	1723vs		1255s	
$Ni(DA)_3(ClO_4)_2$	1723vs		1252s	
$Zn(DA)_3(ClO_4)_2$	1753sh	1718vs	1269s	
$Cd(DA)_3(ClO_4)_2$	1753sh	1718vs	1261s	
$[Co(DA)_2(H_2O)_2](ClO_4)_2$	1750sh	1724vs	1245s	
$[Zn(DA)_2(H_2O)_2](ClO_4)_2$	1752sh	1726vs	1250s	
$Co(DA)_3(H_2O)_2I_2$	1765	1730	1245	1225 [a]
$Co(DA)_4(H_2O)_2I_2$	1760	1727	1240	1225 [a]
$Co(DA)_3(H_2O)_2(NO_3)_2$	1755	1727	1265	1235 [a]
$Ni(DA)_3(H_2O)_2(NO_3)_2$	1760	1730	1255	1228 [a]

[a] From Ref. [11].

fraction patterns were examined for isomorphism. There are marked resemblances between them, though some extra weak bands are observed for the Fe, Co, Ni and Zn complexes. The similarities are consistent with the observed similarity of spectral parameters, but do not indicate complete isomorphism.

3.3. Infrared spectra

The complexes $M(DA)_3(ClO_4)_2$ (M = Mg, Fe, Co, Ni) show (Table 5) only one C=O stretch and one imide III band, shifted slightly down and up, respectively, from the position for *cis*-diacetamide [3]. There is no difficulty in agreeing with the previous assignment [2] that these are due to *cis*-bidentate diacetamide. However $M(DA)_4(H_2O)_2(ClO_4)_2$ (M = Co, Ni) which show two C=O stretches and two imide III bands, were considered to be examples of the less usual monodentate *trans*-diacetamide. The similarity of X-ray powder patterns, ESR and IR spectra shown here between these compounds and $Mg(DA)_4(H_2O)_2(ClO_4)_2$ makes it clear that all these complexes should be formulated $[M(DA)_2(H_2O)_2](ClO_4)_2 \cdot 2DA$. The doubling of the IR frequencies is therefore attributed to the two types of *cis*-diacetamide present, i.e. the coordinated and the hydrogen bonded. By analogy with $M(DA)_3(ClO_4)_2$ it is tempting to assign the lower C=O stretch at 1721–1735 cm^{-1} and the higher imide III band at 1250 ± 3 cm^{-1} to the coordinated ligand; the C=O stretch near 1755 cm^{-1} and the imide III band at 1225 ± 1 cm^{-1} are then due to the hydrogen bonded form. It is likely that some other previously reported complexes [11] also contain both coordinated and hydrogen bonded *cis*-diacetamide (see Table 5) rather than the monodentate ligand.

The compounds $M(DA)_3(ClO_4)_2$ (M = Zn, Cd) and $M(DA)_2(H_2O)_2(ClO_4)_2$ (M = Co, Zn) all show a shoulder on the C=O stretch, but only one imide (III) band, whose position suggests chelation. A possible explanation, consistent with the ESR results, is that the diacetamide molecules are unsymmetrically coordinated, with different M–O bond lengths, as found, for example, for some nitrato complexes [12].

Previously, in the IR spectra of 1:3 complexes some extra bands at 3500, 3342, 1755, 1630 and 1224 cm^{-1} were reported for the incompletely dried samples and were suggested as mainly due to the presence of water [1]. A band near 1755 cm^{-1}, observed for each of these complexes, was associated with a minor modification of the *cis*-diacetamide in the presence of water. Although in most of the complexes this band disappeared after drying in vacuo at room temperature for 24 h, in the spectrum of $Zn(DA)_3(ClO_4)_2$ it did not disappear.

It has been found in this work that the positions of all these extra bands are consistent with those of the corresponding 1:4 complexes and it seems likely that the incompletely dry samples of Mn, Fe, Co and Ni are actually mixtures of the complexes of 1:3 and 1:4 stoichiometries. On drying, in vacuo for 24 h, the 1:4 complexes are converted to 1:3 complexes, a method used here for the preparation of 1:3 complexes.

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