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Seven Coordinate Complexes of Metal(II) Nitrates

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Abstract

ESR spectra at both X and Q band are reported for manganese(II) ions doped into the seven coordinate complexes $M(L)_3(NO_3)_2$ (M = Co, Ni, Zn or Cd; L = pyridine or substituted pyridine). The zero field splitting parameters D and λ ($= E/D$) are deduced. All complexes show considerable deviation from cubic symmetry, as can be expected for a seven coordinate structure. The distinctly lower D value of $Ni(Mn)(pyridine)_3(NO_3)_2$, as compared to the analogous cobalt and zinc complex, suggests a geometry tending towards an octahedral structure. The steric hindrance by the substituent reduces the D value.

Introduction

The complexes $M(pyridine)_3(NO_3)_2$ (M = Zn, Co and Cd) have been shown by X-ray diffraction to have a seven coordinate structure, with coordinated pyridine and bidentate nitrato groups [1, 2]. The corresponding nickel complex is not isomorphous with them, and is thought to have a six coordinate geometry [3]. As part of our investigations of the EPR spectra of manganese(II) ions in different environments, we have studied this ion doped into complexes $M(pyridine)_3(NO_3)_2$, and also in the related complexes of some substituted pyridines, which have not been made previously.

Experimental

Preparation of Complexes

M(pyridine)₃(NO₃)₂ (M = Zn, Cd, Co, Ni)

These were prepared by previously reported methods [4, 5] and had good analyses.

M(3,5-dimethylpyridine)₃(NO₃)₂ (M = Zn, Co, Ni, Cd)

These complexes were prepared by dehydrating the corresponding metal(II) nitrate hexahydrate in 2,2-dimethoxypropane and adding 3,5-dimethylpyridine to the solution while still hot. The precipitates formed were washed with diethyl ether and dried *in vacuo* at room temperature. *Anal.* Found: C, 48.27; H, 5.18; N, 13.55. Calc. for $Zn(3,5\text{-dimethyl-py})_3(NO_3)_2$: C, 49.37; H, 5.29; N, 13.71%. Found: C, 50.02; H, 5.43; N, 13.98. Calc. for $Co(3,5\text{-dimethyl-py})_3(NO_3)_2$: C, 50.00; H, 5.36; N, 13.89%. Found: C, 49.94; H, 5.36; N, 13.78. Calc. for $Ni(3,5\text{-dimethyl-py})_3(NO_3)_2$: C, 50.03; H, 5.36; N, 13.90%.

Co(3,4-dimethylpyridine)₃(NO₃)₂

This complex was prepared by dehydrating cobalt nitrate hexahydrate in 2,2-dimethoxypropane and adding 3 mol of 3,4-dimethylpyridine to the solution. The solution was chilled (−5 °C) for 24 h. The precipitates thus formed were filtered off, washed with diethyl ether and dried *in vacuo* at room temperature. Found: C, 49.92; H, 5.28; N, 13.78. Calc. for $Co(3,4\text{-dimethyl-py})_3(NO_3)_2$: C, 50.00; H, 5.36; N, 13.89%.

Ni(3-methylpyridine)₃(NO₃)₂

This was prepared as described for $Co(3,4\text{-dimethyl-py})_3(NO_3)_2$. Found: C, 46.30; H, 4.47; N, 15.06. Calc. for $Ni(3\text{-methyl-py})_3(NO_3)_2$: C, 46.78; H, 4.55; N, 15.16%.

Zn(3-methylpyridine)₂(NO₃)₂

This was also prepared in a similar manner to that of $Co(3,4\text{-dimethyl-py})_3(NO_3)_2$. Found: C, 38.61; H, 3.67; N, 14.73. Calc. for $Zn(3\text{-methyl-py})_2(NO_3)_2$: C, 38.36; H, 3.73; N, 14.91%.

The normal 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 200D-SRC spectrometer and an ER 078 15-in electromagnet. All samples were measured as polycrystalline solids.

Results

ESR spectra have been obtained at both X and Q bands for Mn(II) ions doped into the compounds

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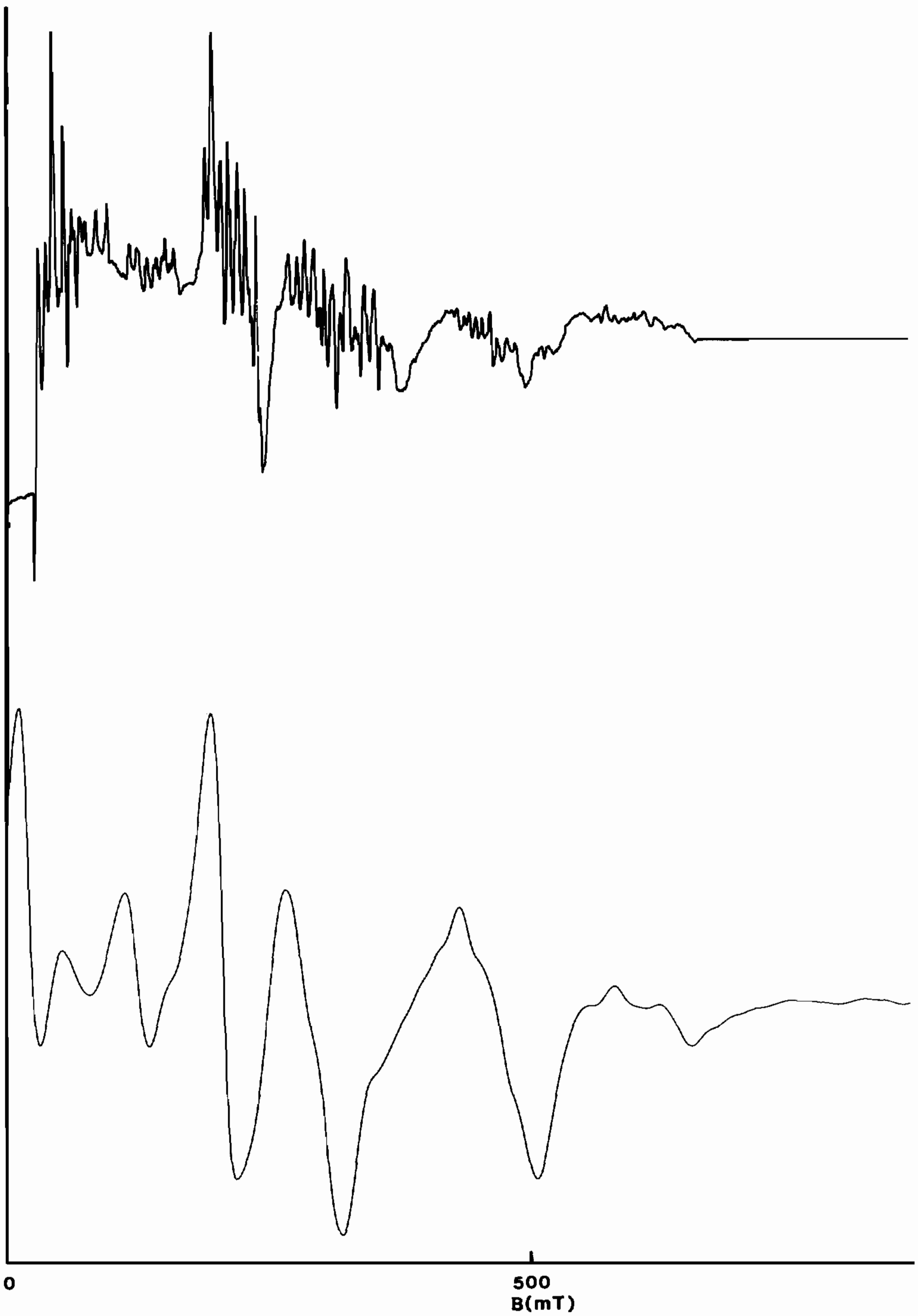

Fig. 1. X band ESR spectrum of $Co(Mn)(3,5\text{-dimethyl-py})_3(NO_3)_2$ and simulated spectrum for $D = 0.130\ cm^{-1}$, $\lambda = 0.059$.

$M(Py)_3(NO_3)_2$ (where M = Co, Ni, Zn and Cd), $M(3,5\text{-dimethyl-py})_3(NO_3)_2$ (where M = Co, Ni, Zn and Cd), $M(3\text{-methyl-py})_3(NO_3)_2$ (where M = Ni and Cd) and $Co(3,4\text{-dimethyl-py})_3(NO_3)_2$.

At X band, all the complexes gave good quality but very complicated spectra (Fig. 1) with considerable overlapping of transitions and detailed interpretation was very difficult. The spectra of $M(py)_3(NO_3)_2$ (M = Co, Zn) were very similar, but considerably different from that of the analogous nickel complex. Strong absorption near zero field was observed for all of these complexes, suggesting D values of about 0.1–0.2 cm^{-1}.

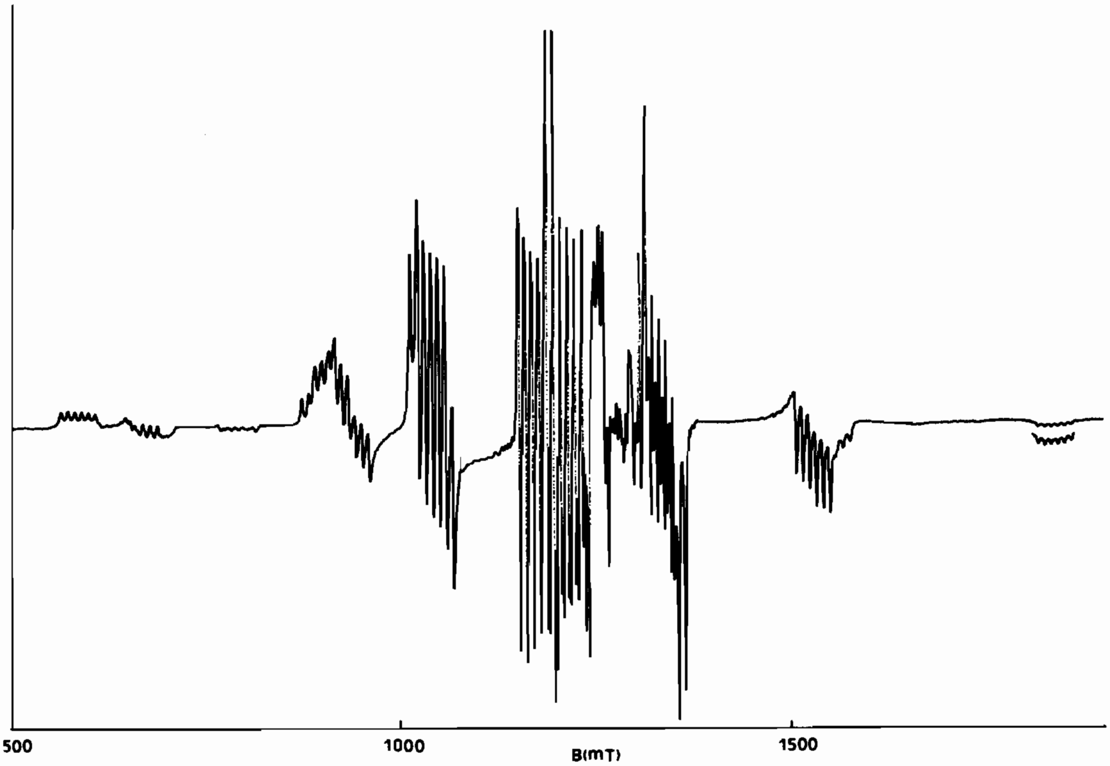

Fig. 2. Q band ESR spectrum of $Zn(Mn)(pyridine)_3(NO_3)_2$.

TABLE I. Q Band ESR Spectrum (mT) of $Co(Mn)(pyridine)_3(NO_3)_2$

Observed (ν = 33.858 GHz)	Calculated for D = 0.148 cm^{-1}, λ = 0.029			
	B	*TP*	Field direction	Levels
579(w)	575.7	5.09	*z*	2- -1
892(m)	892.5	8.09	*z*	3- -2
	892.7	3.79	*y*	6- -5
951(w/m)	949.1	3.75	*x*	6- -5
1025(m)	1022.3	6.75	*y*	5- -4
1047(m)	1045.8	6.71	*x*	5- -4
1168(s)	1167.0	8.55	*x*	4- -3
1172(s)	1172.3	8.53	*y*	4- -3
1209(s)	1209.4	9.04	*z*	4- -3
1319(m/s)	1319.3	8.73	*x*	3- -2
1350(m/s)	1349.9	8.65	*y*	3- -2
1516(m)	1514.4	6.37	*x*	2- -1
1530(m)	1526.4	7.97	*z*	5- -4
1569(w)	1567.1	6.27	*y*	2- -1
1842(w)	1843.5	4.93	*z*	6- -5

Full analysis of the much better resolved Q band spectra (Fig. 2) allowed the determination of D and λ (= E/D) in the Spin Hamiltonian

$$\mathcal{H} = g\beta BS + D(Sz^2 - 1/3S(S+1)) + E(Sx^2 - Sy^2)$$

TABLE II. Q Band ESR Spectrum (mT) of $Ni(Mn)(pyridine)_3(NO_3)_2$

Observed (ν = 33.755 GHz)	Calculated for D = 0.125 cm^{-1}, λ = 0.101			
	B	*TP*	Field direction	Levels
262(w)				
454(w)	455.8	0.14	$\theta = 21°, \phi = 90°$	5- -2
508(w)	509.1	0.03	$\theta = 90°, \phi = 28°$	5- -3
Region of overlap	624.0	0.54	$\theta = 60°, \phi = 00°$	4- -2
	692.0	0.58	$\theta = 64°, \phi = 90°$	4- -2
671(w)	670.3	5.26	*z*	2- -1
873(w)	873.8	4.02	*y*	6- -5
934(w/m)	937.3	8.25	*z*	3- -2
1024(m)	1022.1	7.00	*y*	5- -4
	1040.2	3.87	*x*	6- -5
1093(m)	1093.8	6.89	*x*	5- -4
1171(s)	1170.0	8.70	*x*	4- -3
1183(s)	1182.9	8.65	*y*	4- -3
	1204.7	9.09	*z*	4- -3
1275(s)	1272.6	8.76	*x*	3- -2
1361(m/s)	1361.1	8.54	*y*	3- -2
1407(w)	1407.1	6.26	*x*	2- -1
1477(m)	1473.1	7.89	*z*	5- -4
1566(w)	1563.6	5.99	*y*	2- -1
1744(w)	1742.9	4.80	*z*	6- -5

The results are given in Tables I–III. Because it was not possible to determine the sign of D, assign-

TABLE III. Q Band ESR Spectrum (mT) of Cd(Mn)(pyridine)$_3$(NO$_3$)$_2$

Observed (ν = 34.005 GHz)	Calculated for D = 0.127 cm^{-1}, λ = 0.060			
	B	TP	Field direction	Levels
454.8(w)	455.9	0.12	$\theta = 20^\circ, \phi = 90^\circ$	5--2
511.2(w)				
Region of	641.2	0.57	$\theta = 60^\circ, \phi = 00^\circ$	4--2
overlap	684.7	0.68	$\theta = 60^\circ, \phi = 90^\circ$	4--2
Center *ca.*	671.1	5.15	z	2--1
673.0	751.0	0.49	$\theta = 20^\circ, \phi = 00^\circ$	5--3
	763.4	0.51	$\theta = 20^\circ, \phi = 90^\circ$	5--3
	912.6	3.98	y	6--5
941.0(w/m)	942.7	8.15	z	3--2
	1012.8	3.89	x	6--5
1042.9(m)	1043.5	6.97	y	5--4
1091.6(m)	1086.7	6.90	x	5--4
1180.7(s)	1181.2	8.68	x	4--3
	1188.9	8.65	y	4--3
	1214.4	9.05	z	4--3
	1300.4	8.71	x	3--2
1355.5(m)	1353.7	8.58	y	3--2
1449.7(w)	1450.8	6.21	x	2--1
1489.4(w/m)	1486.4	7.93	z	5--4
1550.8(w)	1545.0	6.05	y	2--1
1757.4(w)	1758.9	4.88	z	6--5

TABLE IV. Q Band ESR Spectrum (mT) of Zn(Mn)(3,5-dimethylpyridine)$_3$(NO$_3$)$_2$

Observed (ν = 33.996 GHz)	Calculated for D = 0.131 cm^{-1}, λ = 0.062			
	B	TP	Field direction	Levels
266				
457(w)	457.4	0.28	$\theta = 16^\circ, \phi = 90^\circ$	5--2
507(w)	506.0	0.01	$\theta = 90^\circ, \phi = 22^\circ$	5--3
Region	643.6	0.60	$\theta = 60^\circ, \phi = 00^\circ$	4--2
of	655.9	5.16	z	2--1
overlap	687.6	0.61	$\theta = 63^\circ, \phi = 90^\circ$	4--2
901(w)	902.9	3.96	y	6--5
933(w/m)	934.8	8.16	z	3--2
1009(w)	1009.4	3.86	x	6--5
1039(m)	1037.7	6.94	y	5--4
1084(m/s)	1083.3	6.87	x	5--4
1188(s)	1187.4	8.63	y	4--3
1215(s)	1214.0	9.06	z	4--3
1298(s)	1300.6	8.72	x	3--2
1358(m/s)	1357.4	8.58	y	3--2
1457(w/m)	1455.6	6.25	x	2--1
1497(m)	1493.5	7.93	z	5--4
1559(w)	1555.6	6.08	y	2--1
1773(w)	1773.6	4.87	z	6--5

TABLE V. Q Band ESR Spectrum (mT) of Ni(Mn)(3-methylpyridine)$_3$(NO$_3$)$_2$

Observed (ν = 33.888 GHz)	Calculated for D = 0.128 cm^{-1}, λ = 0.078			
	B	TP	Field direction	Levels
266(w)				
455(w)	456.6	0.10	$\theta = 18^\circ, \phi = 90^\circ$	5--2
507(w)	507.3	0.02	$\theta = 90^\circ, \phi = 25^\circ$	5--3
Overlapping	635.1	0.57	$\theta = 60^\circ, \phi = 00^\circ$	4--2
of	663.0	5.20	z	2--1
transitions	689.1	0.61	$\theta = 60^\circ, \phi = 00^\circ$	4--2
891(w)	891.2	3.99	y	6--5
934(w/m)	936.3	8.20	z	3--2
1022(w)	1022.5	3.86	x	6--5
1032(m)	1031.4	6.97	y	5--4
1088(m/s)	1087.8	6.88	x	5--4
1176(s)	1175.1	8.68	x	4--3
1185(s)	1185.4	8.64	y	4--3
1211(s)	1209.9	9.07	z	4--3
1288(m/s)	1288.5	8.74	x	3--2
1359(m)	1358.4	8.56	y	3--2
1436(w/m)	1434.4	6.25	x	2--1
1487(m)	1484.1	7.91	z	5--4
1559(w)	1557.8	6.04	y	2--1
1758(w)	1759.1	4.84	z	6--5

ments are made for positive D. Should it be negative the labels would have to be reversed.

In the Q band spectra of most of these complexes the lowest allowed band was overlapped by off-axis (4-2) transitions and the hyperfine structure was less regular than on the other allowed bands.

The positions of off-axis transitions calculated for the Q band spectra of a few complexes fitted very well with those observed. However a weak band observed around 260 mT in the Q band spectra of most of these complexes was not fitted by any of the calculated off-axis transitions.

The complexes of cobalt, nickel and zinc nitrates with dimethyl-substituted pyridines gave spectra very similar to one another, and of the same general type as for the pyridine complexes. Results and assignments are given in Table IV. With cadmium nitrate, again the stoichiometry found was Cd(Mn)L$_3$(NO$_3$)$_2$, but the D value was very much lower. Possibly the larger size of the cadmium ion permits the attainment of a more regular geometry in this case.

With 3-methylpyridine, only nickel and cadmium nitrates gave complexes ML$_3$(NO$_3$)$_2$, and with 4-methylpyridine no complexes were obtained. The spectra of M(Mn)(3-methylpyridine)$_3$(NO$_3$)$_2$ (M = Ni or Cd) (Table V) were again clearly similar to those of the dimethylpyridine complexes of cobalt, nickel and zinc nitrates.

Discussion

Values of D and λ for all of the complexes are listed in Table VI. All showed considerable deviation

TALBE VI. Zfs Parameters of Mn(II) in the Complexes

Complex	D (cm^{-1})	λ
Zn(pyridine)$_3$(NO$_3$)$_2$	0.147	0.014
Co(pyridine)$_3$(NO$_3$)$_2$	0.148	0.029
Ni(pyridine)$_3$(NO$_3$)$_2$	0.125	0.101
Cd(pyridine)$_3$(NO$_3$)$_2$	0.127	0.060
Zn(3,5-dimethylpyridine)$_3$(NO$_3$)$_2$	0.131	0.062
Co(3,5-dimethylpyridine)$_3$(NO$_3$)$_2$	0.130	0.059
Ni(3,5-dimethylpyridine)$_3$(NO$_3$)$_2$	0.130	0.065
Cd(3,5-dimethylpyridine)$_3$(NO$_3$)$_2$	0.070	0.020
Co(3,4-dimethylpyridine)$_3$(NO$_3$)$_2$	0.125	0.065
Ni(3-methylpyridine)$_3$(NO$_3$)$_2$	0.128	0.078
Cd(3-methylpyridine)$_3$(NO$_3$)$_2$	0.127	0.105

from cubic symmetry, as would be expected for a seven coordinate structure. The similarity of structure between M(pyridine)$_3$(NO$_3$)$_2$ (M = Co, Zn) shows clearly in their spectra, and the slightly lower D value found for the cadmium complex is in line with the usual observation that D decreases as the size of the host ion increases.

The nickel analogue, whilst apparently retaining a generally similar structure, has a distinctly lower D value than the cobalt and zinc complexes, suggesting a geometry tending towards an octahedral structure, but with an increased rhombicity. This confirms the previous observations on its structure, but shows that there is still considerable distortion.

The dimethylpyridine complexes of cobalt, nickel and zinc have approximately the same values of D and λ, suggesting that their structures are closely similar. The somewhat lower D values, compared with the pyridine complexes of cobalt and zinc, are the opposite of what would be expected from the increased basicity of the ligands. It seems likely that steric factors are causing an increase in the length of the metal–nitrogen bonds, and hence a decrease in the difference between the nitrogen and oxygen donors. A similar effect was found for complexes of these ligands with cadmium halides [6].

However the general similarity of the spectra of these complexes to those of pyridine indicates that they all very probably have the same type of seven coordination.

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