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ESR Spectra of a Seven-coordinated Pentagonal Bipyramidal Manganese(II) Complex

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Until recently seven-coordination was rare for first-row transition metal complexes. The seven-coordinated pentagonal bipyramidal geometry is now obtainable by using the ligand 2,6-diacetylpyridine-bis(semicarbazone) or DAPSC as shown in Fig. 1. This structure was confirmed by X-ray analysis [1].

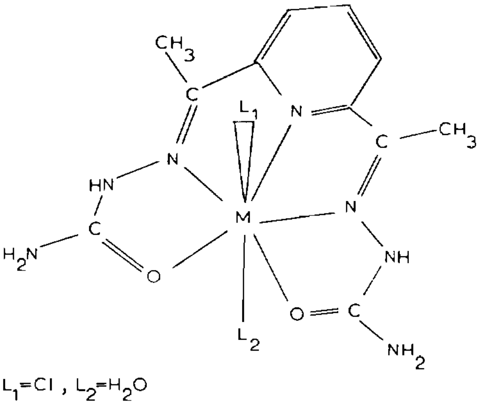

Fig. 1. Pentagonal bipyramidal geometry adopted by metal ions complexed with DAPSC ligand.

The ground state for high spin Mn(II) ion is ^{6}S and there are no other sextet states. Thus, there are no spin-allowed or La Porte allowed d–d transitions. Second-order spin–orbit effects couple the excited ^{4}T state with the ground ^{6}S state. Zero field splitting produces three Kramer's doublets ($M_s = \pm 5/2, \pm 3/2, \pm 1/2$). If the zero-field splitting is small, then the applied magnetic field in an electron spin resonance (ESR) experiment splits each Kramer doublet into two singlets resulting in five transitions. Each transition line is further split by manganese nuclear hyperfine interactions ($I = 5/2$) which results, in principle, in a thirty line spectrum [2, 3]. Our study is the first report of an ESR spectrum of a confirmed pentagonal bipyramidal Mn(II) complex with resolved hyperfine structure. Van Heuvelen *et al.* [4] reported the ESR spectra of pentagonal bipyramidal Mn(II) complexes that exhibited only single line spectra. Also, the ESR spectra of cobalt [5] and copper [6] seven-coordinated pentagonal bipyramidal complexes have been reported.

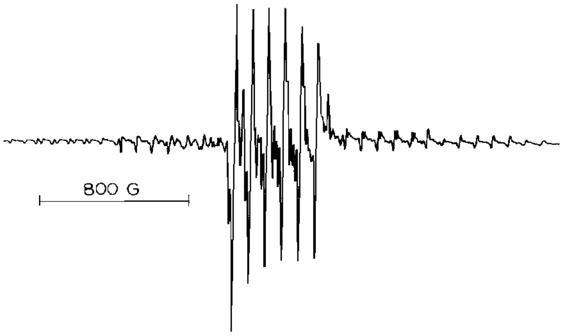

Fig. 2. Q-band ESR spectrum of powdered sample of {Zn-(Mn)(DAPSC)(H_2O)(Cl)}Cl·2H_2O.

Experimental

The manganese(II) complex, {Mn(DAPSC)(H_2O)-(Cl)}Cl·2H_2O, was prepared by the literature method [7]. Single crystals of Mn(II) doped into the isomorphous complex {Zn(DAPSC)(H_2O)(Cl)}Cl·2H_2O were grown by slow evaporation of ethanol solution containing 0.1% manganese chloride and 99.9% zinc chloride. ESR spectra at 298 K were obtained with a Varian E4 at X-band or with a Varian E9 at Q-band. The complexes were ground to a powder for the ESR measurements. Magnetic susceptibilities at 298 K were determined by the Guoy method.

Results and Discussion

In Fig. 2, the first derivative Q-band ESR spectrum of Mn-doped Zn complex consists of five groups of six lines centered at $g = 2.00$ corresponding to the five allowed electronic transitions split into six lines by hyperfine interaction with the ^{55}Mn nucleus. This hyperfine splitting of 90 ± 1 G was found from analysis of the Q-band spectrum spectra, with second-order corrections. The zero-field splitting parameter, D, was estimated to be 0.02 cm^{-1} by two methods. Tikhomirova *et al.* [8] observed a linear relationship between D^2 and the difference between the width of the first and sixth Mn hyperfine lines. Eidels-Dubovoi and Beltran-Lopez [9] plotted the relationship between the intensity ratios $I_{-5/2}/I_{-3/2}$ and $I_{-5/2}/I_{-1/2}$ for the low fields $M_s = +\frac{1}{2} - \rightarrow \frac{1}{2}$ lines as a function of D/H_0. Comparison of the spacings of the hyperfine components in the highfield and low-field sets suggests that D and A have the opposite signs [10], so that D is probably positive.

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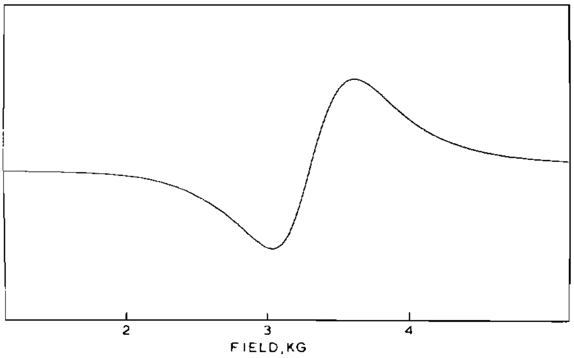

Fig. 3. X-band ESR spectrum of powdered sample of undiluted $\{Mn(DAPSC)(H_2O)(Cl)\}Cl\cdot 2H_2O$.

The magnetic moment of the Mn(DAPSC) complex is 5.01 BM which is close to value of 5.92 BM predicted for high spin manganese(II) with a spin of 5/2. This magnetic moment is in agreement with the ESR results.

The ESR spectrum of $\{Mn(DAPSC)(H_2O)(Cl)\}Cl\cdot 2H_2O$ is somewhat different from the reported ESR spectra [4] of other Mn(II) complexes thought to be seven-coordinate: $MnBCL_2\cdot 6H_2O$, $MnBCl_2\cdot H_2O$, and $MnBCl_2$ where B is 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-{12.3.1}octadeca-1(18),2,12,14,16-pentaene. The hexahydrate exhibited a five line ESR spectrum while the other two exhibited a single line spectrum. As all three spectra were run on undiluted samples, the observed spectra could result from spin-exchange between neighboring manganese atoms which would wipe out the hyperfine detail in these spectra. As seen in Fig. 3, an undiluted sample of $\{Mn(DAPSC)(H_2O)(Cl)\}Cl\cdot 2H_2O$ also resulted in an ESR spectrum which consisted of a single line.

In conclusion, by comparison with ESR data for six-coordinated Mn complexes [10, 11, 12], it is apparent that our spectrum can be interpreted as arising from a nearly undistorted 'pseudo-octahedral' complex.

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