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# Large Zero-Field Splitting for Manganese(II) in a Trinuclear (Pt, Mn, Pt) Complex of 1-Methylthymine

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The anti-tumour activity of *cis*-$Pt(NH_3)_2Cl_2$ has led to a surge of interest in the synthesis of a wide range of Pt(II) compounds. Of particular interest are the polynuclear complexes in which two or more platinum atoms are brought into close proximity by appropriately chosen ligands, generally heterocyclic bases [1–3]. Studies on these polynuclear systems have been further stimulated by the fact that some of them, the 'blues', are paramagnetic [2]. As is often the case, the question arises as to what extent a given Pt–Pt distance is dictated by the geometry of the bridging ligands and/or by any degree of Pt–Pt bonding.

The recent isolation [4] of a heterotrinuclear complex, bis[bis($\mu$-1-methylthyminato)*cis*-diammine-platinum(II)] manganese(II) dichloride decahydrate, containing a linear $Pt^{II}$–$Mn^{II}$–$Pt^{II}$ array with a Pt–Mn distance of 2.704 Å, has provided the interesting opportunity of studying the effects on the central $Mn^{2+}$ ion of the axially disposed Pt atoms. The essential features of the coordination geometry about the $Mn^{2+}$ ion in this complex (hereafter referred to as $Pt_2Mn$) are summarised in Table I.

TABLE I. Bond Lengths and Angles about Mn[a].

| | | | |
|---|---|---|---|
| Mn–Pt | 2.704 Å | O–Mn–O′ | 94.5° |
| Mn–O | 2.103 | Pt–Mn–O | 82.2 |
| Mn–O′ | 2.158 | Pt–Mn–O′ | 101.1 |

[a] Data from reference 4.

Departures from cubic symmetry in the ligand field about high spin $Mn^{2+}$ can be readily studied by e.p.r. and derivation therefrom of the zero-field splitting parameters D and E [5]. The parameter $\lambda$ (= E/D) is generally used in the associated calculations.

The X-band (9.50 GHz) spectrum of a polycrystalline sample of $Pt_2Mn$ (Fig. 1A) is remarkably simple, consisting of a strong band at 121.3 mT. Such a spectrum is consistent with a very high D value and a low $\lambda$ value.

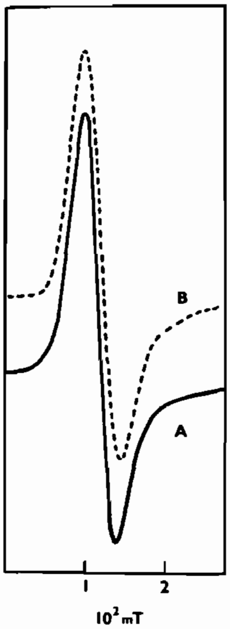

Fig. 1. X-band (9.50 GHz) spectrum of the $Pt_2Mn$ complex. A, experimental spectrum; B, simulated spectrum with D = 1.9 $cm^{-1}$, $\lambda$ = 0.026.

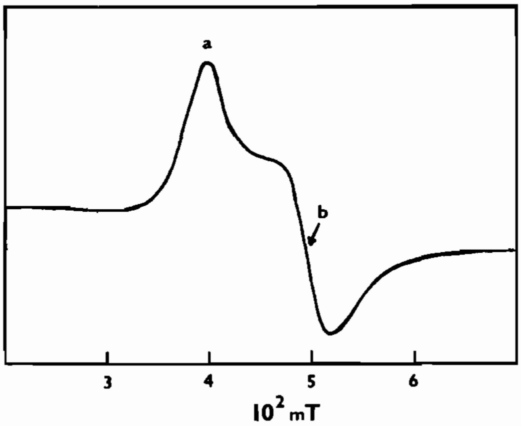

Fig. 2 Q-band (35.98 GHz) spectrum of the $Pt_2Mn$ complex

The assymmetry in the derivative peak heights suggested that $\lambda \neq 0$. Changing the microwave frequency to Q-band (35.98 GHz) permitted the resolution of the band into two components at 399.3 and 496.2 mT (Fig. 2), taken at peak a and crossover b respectively. The Q-band spectrum also showed a very weak band at ~1310 mT.

Analysis of the Q-band using the programme ESRS [6] gave D = 1.9 $cm^{-1}$ and $\lambda$ = 0.026 (Table II). These parameters predict the corresponding low field y and x components to be at 102.8 and 126.7 mT

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TABLE II. Q-Band (35.98 GHz) Spectrum (mT) of the $Pt_2Mn$ Complex.

| Observed | Calc for $D = 1.9$ cm$^{-1}$, $\lambda = 0.026$ | Axis |
|---|---|---|
| 399.3 | 396.1 | y |
| 496.3 | 491.9 | x |
| ~1310[a] | 1311 | z |

[a]Very weak band.

respectively at X-band frequency, but a numerical check was not possible in this case because the individual bands were not resolved. A simulation of the X-band spectrum (1B) using these parameters is, however, in good agreement with the experimental spectrum.

The evaluation of $\lambda$ depends mainly upon the separation of the components of the low field band, which from the Q-band results can be measured with reasonable accuracy. The low value obtained agrees well with the small rhombic distortion about $Mn^{2+}$ found from the crystallographic study [4] Table I).

D cannot be determined to the same precision as the spectra contain so few bands and because at high D values the resonance fields of the x and y components are not very sensitive to D.

We do not expect D to be significantly lower than the value of 1.9 cm$^{-1}$ found, as high field bands showing pronounced D-dependence should then be observed [7, 8]. At large D values these transitions move to field values beyond the range of conventional spectrometers.

Even if the measured D value of 1.9 cm$^{-1}$ were to be slightly low it is still significantly larger than the values reported in the literature for other very strongly distorted six coordinate manganese(II) compounds (*e.g.*, for the *trans*-$N_4I_2$ donor set in Zn(Mn) $(N_2H_4)_2I_2$ D = 1.21 [8], and for the *trans*-$O_4I_2$ donor set in $[Zn(Mn)]_3B_7IO_{13}$ D = 0.624 [9]).

The Mn–O distances observed [4] for $Pt_2Mn$ are quite normal and the in-plane ligand field about $Mn^{2+}$ would be expected to be slightly weaker than that generated by four nitrogen donor atoms in compounds such as $M(N_2H_4)_2I_2$ [8] or M(4-Me-pyridine)$_4I_2$ [7]. We conclude therefore that the presence of platinum(II) in axial positions in $Pt_2Mn$ produces a significantly greater tetragonal distortion than those present in well-established $MnN_4I_2$ or $MnO_4I_2$ coordination spheres.

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