

The X-Ray Structure of a Heteronuclear (Pt, Mn) Complex of 1-Methylthymine and its Vibrational Spectra

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A heteronuclear complex of 1-methylthymine containing both $\text{cis-Pt}(\text{NH}_3)_2^{2+}$ and Mn^{2+} has been prepared and its structure determined by X-ray diffraction. $\text{Mn}[\text{Pt}(\text{NH}_3)_2(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2]_2\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ crystallizes in space group $P\bar{1}$ with cell parameters $a = 11.788(6)$ Å, $b = 10.035(5)$ Å, $c = 10.983(6)$ Å, $\alpha = 115.16(3)$, $\beta = 103.22(4)$, $\gamma = 77.39(4)^\circ$, $Z = 1$. The structure was refined on 2846 reflections to $R_1 = 0.077$ and $R_2 = 0.088$. Binding of $\text{cis-Pt}(\text{NH}_3)_2^{2+}$ occurs through N3, binding of Mn^{2+} through an exocyclic oxygen of each thymine ligand. Both Pt and Mn have square planar coordinations with Mn in the inversion centre of the trinuclear Pt_2Mn unit. The Pt–Mn distance within the cation is $2.704(1)$ Å. Complex formation between the bis(1-methylthyminato)platinum complex and Mn^{2+} in aqueous solution has been followed using Raman spectroscopy. The effects of covalent Mn binding on the most intense heterocyclic ring vibrations has been studied. Solid state IR and Raman spectra were examined with regard to the question concerning the donor atoms of Mn (O4 and/or O2), since X-ray crystallography, because of the pseudo-twofold axis through N3 and C6 of the 1-methylthymine ligand, could not give a definitive answer. Mn binding is believed to occur through O4 of the thymine ligands.

Introduction

Platinum(II) binding to N3 of the model nucleobase 1-methylthymine promotes binding of a second metal Pt(II) [1, 2], Ag(I) [3] or a proton [4] through an exocyclic oxygen of this ligand. We have recently demonstrated this using X-ray analysis, IR, UV, and $^1\text{H-NMR}$ spectroscopy. Guay and Beauchamp [5], in a study on the interaction of Ag(I) with uridine, reported the X-ray structure of a 2:2 silver-(1-methylthymine) complex with Ag(I) binding strongly to N3, moderately to O4 and weakly to O2.

It should be interesting to know whether these observations are restricted to platinum and silver, or are a general consequence of metal binding to the N3 position of N1 substituted pyrimidine-2,4 diones. If so, the binding of metal cations with either beneficial or deleterious effects on biological systems should be of particular interest in this respect. For this purpose we have studied the interaction between bis(1-methylthyminato)cis-diammineplatinum(II) and manganese(II) in aqueous solution using Raman spectroscopy. A trinuclear complex, bis [bis(μ -1-methylthyminato)cis-diammineplatinum(II)] manganese(II) dichloride decahydrate, $\text{Mn}[\text{Pt}(\text{NH}_3)_2(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2]_2\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, has been isolated and its structure determined by X-ray crystallography.

Experimental

The title compound was obtained after addition of one equivalent of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ to an aqueous solution of bis(1-methylthyminato)cis-diammineplatinum(II) [1, 3] and subsequent slow evaporation at 4°C (pH = 6.0). Yield 60%. The yield increased to 85–90% with 2 equivalents of Mn per Pt. Recrystallization from an aqueous solution containing a fourfold excess of MnCl_2 over the title compound did not give any indication of a second species besides the Pt_2Mn compound. The compound crystallizes as colorless, transparent columns, which tend to crack and partially lose water of crystallization when kept on air. *Anal.* Found: C, 22.25; H, 4.61; N, 12.61; O, 21.53; Cl, 5.31; Mn, 4.21. Calcd. for $\text{C}_{24}\text{H}_{60}\text{N}_{12}\text{O}_{18}\text{Cl}_2\text{MnPt}_2$ (decahydrate): C, 21.82; H, 4.59; N, 12.73; O, 21.80; Cl, 5.37; Mn, 4.16. Density measurements (*vide infra*) agree with formulation as a decahydrate. The crystal data are: $a = 11.788(6)$, $b = 10.035(5)$, $c = 10.983(6)$ Å, $\alpha = 115.16(3)$, $\beta = 103.22(4)$, $\gamma = 77.39(4)^\circ$, $V = 1134$ Å³, space group $P\bar{1}$, $Z = 1$, mol. wt. 1321, $D_c = 1.934$, $D_m = 1.945$ g cm⁻³, $\mu_{\text{Mo-K}\alpha} = 69.6$ cm⁻¹. The cell parameters were determined by precession photographs and refined by centering 15 reflections on a Syntex P2₁ diffractometer. For intensity data

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TABLE I. Atomic Coordinates and Thermal Parameters. The Anisotropic Temperature Factor is of the Form: $T = \exp[-\frac{1}{2}(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$; B_{ij} in \AA^2 .

Atom	x/a	y/b	z/c
Mn	0	0	0
Pt	-0.0135(1)	-0.2840(1)	-0.0478(1)
N3	0.158(2)	-0.326(2)	-0.068(2)
C4	0.209(2)	-0.470(3)	-0.111(2)
O4	0.146(1)	-0.570(2)	-0.133(2)
C5	0.321(2)	-0.508(2)	-0.136(2)
C7	0.373(2)	-0.671(3)	-0.187(3)
C6	0.389(2)	-0.399(3)	-0.110(2)
N1	0.337(2)	-0.254(2)	-0.062(2)
C1	0.416(2)	-0.137(4)	-0.038(3)
C2	0.229(2)	-0.216(2)	-0.042(2)
O2	0.180(1)	-0.080(2)	0.002(2)
N3A	-0.062(2)	-0.311(2)	-0.245(2)
C4A	-0.116(2)	-0.450(2)	-0.326(2)
O4A	-0.130(1)	-0.531(2)	-0.278(2)
C5A	-0.155(2)	-0.476(2)	-0.467(2)
C7A	-0.211(2)	-0.611(3)	-0.554(2)
C6A	-0.139(2)	-0.380(3)	-0.518(2)
N1A	-0.092(2)	-0.251(3)	-0.435(2)
C1A	-0.085(2)	-0.144(3)	-0.496(2)
C2A	-0.055(2)	-0.218(2)	-0.291(2)
O2A	-0.013(2)	-0.103(2)	-0.219(2)
N2	-0.188(1)	-0.243(2)	-0.025(2)
N4	0.032(2)	-0.262(2)	0.148(2)
CL	-0.183(2)	-0.018(2)	0.253(2)
O20	0.316(2)	0.873(2)	0.300(2)
O21	0.363(2)	0.197(3)	0.286(2)
O23	0.343(3)	0.556(4)	0.215(4)
O24	0.634(3)	0.087(4)	0.390(3)
O22	0.512(3)	0.611(6)	0.451(7)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	3.1(2)	1.7(2)	1.6(2)	-0.5(2)	0.1(2)	0.8(2)
Pt	2.53(4)	1.99(4)	1.22(3)	-0.56(2)	-0.07(2)	0.90(3)
N3	6.2(11)	0.5(7)	1.6(7)	-0.5(7)	1.5(7)	-0.1(6)
C4	1.4(9)	5.2(13)	2.0(9)	-1.2(9)	-0.1(7)	1.4(9)
O4	3.9(8)	2.9(7)	3.4(7)	-1.0(6)	0.1(6)	1.5(6)
C5	3.3(10)	2.6(8)	2.8(9)	0.8(7)	0.6(7)	0.4(7)
C7	4.8(13)	2.5(11)	6.6(16)	1.9(10)	3.0(12)	1.3(11)
C6	3.1(11)	3.6(12)	3.5(11)	-2.5(9)	-1.2(9)	2.0(9)
N1	4.8(12)	4.1(11)	2.3(9)	-1.4(9)	-0.5(8)	0.9(8)
C1	3.6(13)	8.8(20)	4.9(15)	-2.6(13)	-0.1(11)	2.7(14)
C2	4.3(12)	1.5(10)	2.3(9)	0.4(9)	0.5(9)	1.8(8)
O2	4.7(8)	1.9(7)	3.8(8)	-0.8(6)	0.5(6)	0.9(6)
N3A	4.4(10)	4.0(10)	1.7(8)	1.8(8)	0.6(7)	2.1(8)
C4A	1.6(9)	1.7(9)	3.3(11)	-0.9(7)	-0.8(7)	0.9(8)
O4A	5.4(9)	3.4(8)	3.3(8)	-2.0(7)	-1.0(6)	2.1(7)
C5A	6.0(12)	2.1(8)	2.6(9)	-1.1(8)	0.3(8)	0.5(7)
C7A	4.4(13)	3.4(12)	3.3(12)	-1.2(10)	-1.0(10)	-0.0(10)
C6A	4.0(12)	3.2(12)	3.0(11)	-0.5(9)	-0.3(9)	1.0(10)
N1A	7.7(14)	5.2(12)	2.8(10)	-0.4(11)	1.7(10)	2.1(9)
C1A	7.2(16)	4.2(13)	3.4(12)	-1.0(11)	1.3(11)	2.6(11)
C2A	2.8(10)	2.7(10)	1.9(9)	-0.3(8)	0.2(8)	1.1(9)
O2A	5.4(9)	2.8(7)	1.4(6)	-0.8(7)	-0.3(6)	0.9(6)
N2						

(continued on facing page)

TABLE I. (continued)

Atom	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
N2	2.7(8)	3.5(9)	2.8(9)	-0.9(7)	0.3(7)	0.8(7)
N4	4.9(10)	5.1(11)	4.6(11)	0.4(8)	0.7(8)	5.3(10)
CL	18.2(15)	20.6(17)	14.0(13)	-0.3(12)	2.0(11)	8.8(12)
O20	11.0(16)	6.7(12)	3.9(10)	1.3(11)	2.9(10)	1.9(9)
O21	7.4(13)	13.9(20)	5.1(12)	5.5(13)	3.2(10)	4.4(13)
O23	10.8(21)	14.3(25)	16.6(29)	-4.3(19)	6.0(20)	3.5(22)
O24	9.0(17)	14.7(25)	12.2(24)	1.7(16)	3.7(16)	6.4(21)
O22	8.7(22)	27.8(51)	40.9(76)	-3.8(27)	-5.0(33)	24.4(56)

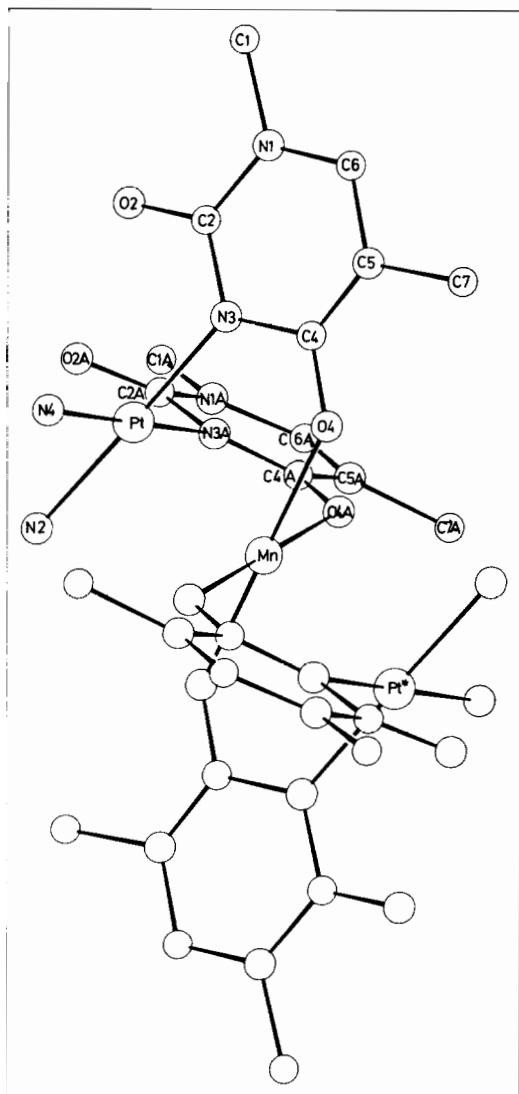


Fig. 1. The molecular cation of bis[bis(μ -1-methylthyminato)*cis*-diammine platinum(II)] manganese(II) dichloride decahydrate.

collection (3129 independent reflections, $2^\circ \leq 2\theta \leq 48^\circ$, ω -scan) Mo- K_α radiation (graphite monochromator, $\lambda = 0.71069 \text{ \AA}$) was used. Lorentz, polariza-

TABLE II. Distances and Angles around the Metal Atoms.

Distances			
Pt-N(3)	2.016(20)	Mn-O(4)	2.103(17)
Pt-N(3A)	2.022(17)	Mn-O(4A)	2.158(14)
Pt-N(2)	2.055(19)		
Pt-N(4)	2.022(20)		
Pt-Mn	2.704(1)		
Angles			
N(3)-Pt-N(3A)	91.2(8)	O(4)-Mn-O(4A)	94.5(6)
N(3)-Pt-N(2)	179.2(7)	Pt-Mn-O(4)	82.2(4)
N(3)-Pt-N(4)	89.9(8)	Pt-Mn-O(4A)	101.1(4)
N(3A)-Pt-N(2)	89.5(8)		
N(3A)-Pt-N(4)	178.2(8)		
N(2)-Pt-N(4)	89.4(8)		
Mn-Pt-N(3)	86.0(5)		
Mn-Pt-N(3A)	85.2(6)		
Mn-Pt-N(2)	94.5(5)		
Mn-Pt-N(4)	96.3(6)		

tion and an empirical absorption correction were applied. The structure was solved by the Patterson method and refined by full matrix least squares with anisotropic thermal parameters. Hydrogen atoms were not located. Final R values were $R_1 = 0.077$ and $R_2 = 0.088$ for 2846 reflections with $F_o \geq 3.92 \sigma(F_o)$.

IR spectra were recorded on a Perkin Elmer 580 grating spectrometer with a maximum resolution of 1.3 cm^{-1} (extended scale) as Nujol mulls. Calibration against polystyrene.

Raman spectra were recorded on a Coderg PH1 with krypton laser excitation (647.1 nm). A plasma filter was used, and wavenumber calibration was achieved by means of indene. Slit widths as indicated.

Structure

The trinuclear cation of bis[bis(μ -1-methylthyminato)*cis*-diammineplatinum(II)]manganese(II) dichlor-

ide decahydrate is shown in Fig. 1. The atomic parameters are listed in Table I, interatomic distances and angles around the heavy metal atoms in Table II. Each platinum is coordinated by two NH_3 groups *cis* to each other and two N3 atoms of the 1-methylthymine ligands, thus leading to the usual square planar coordination of Pt(II). There is no significant deviation from exact planarity, including the Pt atom. The molecular cation shows crystallographic centrosymmetry with the manganese sitting in the inversion centre. Manganese(II) therefore has a strict square planar coordination sphere by space group symmetry with four oxygen donor atoms, one from each thymine ligand. As with other 1-methylthymine complexes [1–3], there is an ambiguity with respect to the donor atoms of Mn because of the pseudo two-fold axis through N3 and C6 of the ligand. Thus the question arises whether O2 or O4 are coordinating. There is good evidence suggesting that O4 is the best nucleophilic site once N3 is bound to a metal [2, 5] and that O2 is only weakly basic [5]. We therefore tentatively assign O4 as the donor atom of Mn(II) in the here described compound, even though we cannot differentiate between N1 and C5 crystallographically. It should be pointed out, that the vibrational spectra (*vide infra*) can be interpreted satisfactory in terms of a single type of bridge (either N3, O4 or N3, O2) being present rather than two different ones (N3, O4 and N3, O2).

Pt– NH_3 (2.06(2), 2.02(2) Å) and Pt–N3 (1-methylthymine) distances (2.02(2) Å) are similar to those reported before for related compounds [1, 3]. The Mn–O distances (2.10(2), 2.16(1) Å) are within the range found for octahedral complexes with keto oxygen atoms coordinating to Mn(II) [6].

The distance between Pt and Mn within the cation is 2.704(1) Å compared to 2.849(1) Å in the $\text{Pt}_2\text{-Ag}$ compound [3] and to 2.909(3) Å and 2.974(1) Å in the head-to-head and head-to-tail platinum (1-methylthymine) dimers [1, 2]. The shorter distance of the metal centres in the Pt_2Mn compound probably is a consequence of both the square planar coordination of Mn(II) which enables its closer approach to the Pt atoms than in the tetrahedral arrangement of Ag(I) in the Pt_2Ag complex, and the smaller atomic radius of Mn. The distance between nearest Pt atoms of adjacent cations (symmetry operation $-x, 1-y, -z$) is 4.807 Å, and the angle Pt–Pt–Mn is 158.4°. Certainly, there is no intermolecular interaction between adjacent Pt centres under these conditions.

The Pt–Mn–Pt axis, which is linear by space group symmetry, is roughly perpendicular to both the coordination planes of Pt and Mn. These planes are tilted towards each other by an angle of 20.1°, compared with 29.5° and 36.1° in the pla-

tinum dimers [1, 2], where larger radii of the metals cause a stronger tilting of the coordination planes.

Both 1-methylthymine ligands are planar within the standard deviations. Their normals include an angle of 89.2°. The Pt atom deviates slightly from these planes (0.116 and 0.016 Å, respectively) compared with mean 0.21 Å in the Pt_2Ag complex [3] and 0.30 Å in a bis(1-methylthyminato-N3) complex of Hg(II) [7]. In contrast, the position of the Mn(II) atom deviates markedly from the ligand planes: it is 0.42 Å and 0.66 Å above or below the 1-methylthymine planes. With the covalent binding character of Mn and 1-methylthymine deduced from the vibrational spectra (*vide infra*), this implies substantial contributions of iminolate resonance structures of the type $\text{C}=\text{O}^-$ to the original keto oxygen structure $\text{C}=\text{O}$ of neutral 1-methylthymine.

Angles between normals of the ligand planes and the coordination plane of Pt are 88.3° and 70.7°, respectively. Standard deviations for intra(1-methylthymine) ligand bond lengths and angles are too large to justify a detailed discussion.

The crystal contains five water molecules per asymmetric unit as deduced from observed and calculated densities. Two of the water molecules, as well as the chloride ions, exhibit very large thermal parameters, indicating strong thermal motion within the crystal or a partial disorder. The chloride ion in the asymmetric unit is hydrogen bonded to O24 with a distance of 2.68 Å.

Vibrational Spectra

Manganese binding to $\text{cis-Pt}(\text{NH}_3)_2(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2$ in aqueous solution can be inferred from Raman spectroscopic changes of 1-methylthymine modes. Thus, shifts of some of the very intense in-plane (A') modes of 1-methylthymine ligands in $\text{cis-Pt}(\text{NH}_3)_2(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2$ are observed when Mn(II) is added to the solution (Fig. 2).

For example, the ring-breathing mode of 1-methylthymine [8], which absorbs at 788 cm^{-1} in the anion and at 791 cm^{-1} in the 2:1 platinum complex, is shifted to 802 cm^{-1} when Mn(II) is bound as well. The ring-stretching mode at 1277 cm^{-1} (potassium salt of 1-methylthymine) is shifted to 1242 cm^{-1} with Pt coordinated (2:1 complex) and to 1250 cm^{-1} upon simultaneous Pt_2 , Mn binding. The 1219 cm^{-1} band of the bis(1-methylthyminato)-platinum(II) complex is also shifted in the Pt_2Mn complex (1224 cm^{-1}) and, at the same time, increases in intensity. Interestingly, in the head-to-head platinum(II) dimer bis(μ -1-methylthyminato-N3,O4)-bis(*cis*-diammineplatinum(II)) dinitrate, the separation

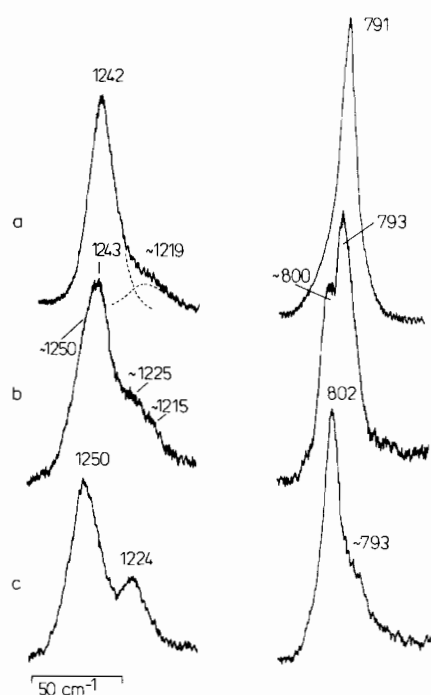


Fig. 2. Raman solution (H_2O) spectra around 800 and 1250 cm^{-1} of a) $\text{cis-Pt}(\text{NH}_3)_2\text{T}_2$; b) $\text{cis-Pt}(\text{NH}_3)_2\text{T}_2 + 0.5\text{ MnCl}_2$; c) $\text{cis-Pt}(\text{NH}_3)_2\text{T}_2 + 2\text{ MnCl}_2$; slit width 4 cm^{-1} ; $c_{\text{Pt}} = 0.2\text{ M}$.

of this band (1209 cm^{-1}) from that of the ring-stretch (1252 cm^{-1}) has further increased and the intensity of the 1209 cm^{-1} band has reached that of the 1253 cm^{-1} band.

Though some of the weaker Raman bands of $\text{cis-Pt}(\text{NH}_3)_2(\text{C}_6\text{H}_7\text{N}_2\text{O}_2)_2$ are shifted upon $\text{Mn}(\text{II})$ binding as well, the three other very intense modes around 540 cm^{-1} (ring-deformation), 1370 cm^{-1} (ring-stretch + $(\text{N}-\text{CH}_3)$ deformation), and 1660 cm^{-1} ($\text{C}=\text{C}$ stretch) are rather insensitive towards additional metal binding. The $1500\text{--}1600\text{ cm}^{-1}$ region which, in the solid state infrared spectrum, undergoes the most prominent changes upon additional metal binding [2] or protonation [3], in the Raman solution spectrum does not give any strong indication of metal binding due to the broadness and general weakness of the bands in this range. Thus Raman spectroscopy appears to be a good indicator of metal binding with regard to some typical ring modes, but not with regard to vibrations of functional groups and/or more or less localized modes.

The spectral changes observed upon variation of the $\text{Pt}:\text{Mn}$ ratio indicate that the equilibrium $2\text{ cis-Pt}(\text{NH}_3)_2\text{T}_2 + \text{Mn}^{2+} \rightleftharpoons \text{cis-}[\text{Pt}(\text{NH}_3)_2\text{T}_2\text{MnT}_2\text{-Pt}(\text{NH}_3)_2]^{2+}$ ($\text{T} = 1\text{-methylthymine anion}$) in aqueous solution lies clearly on the left side.

Covalent binding of $\text{Mn}(\text{II})$ to the bis(1-methyl-

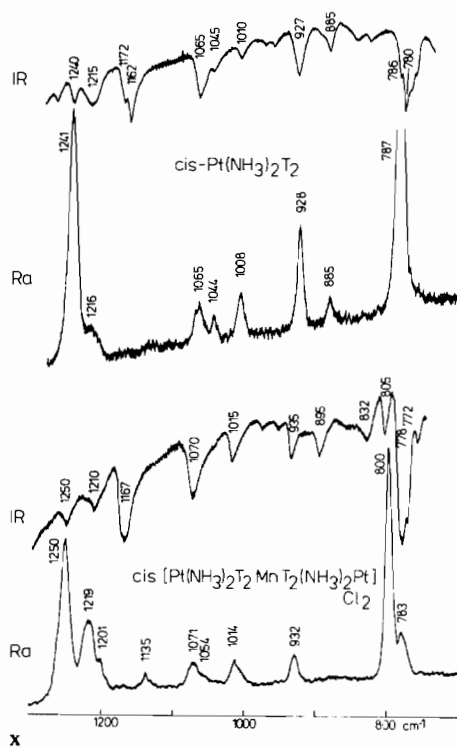


Fig. 3. Solid state IR and Raman spectra of $\text{cis-Pt}(\text{NH}_3)_2\text{T}_2$ aq and $\text{cis-}[(\text{NH}_3)_2\text{PtT}_2\text{MnT}_2\text{Pt}(\text{NH}_3)_2]\text{Cl}_2 \cdot 10\text{H}_2\text{O}$ between 750 and 1250 cm^{-1} . Slit width (Ra) 4 cm^{-1} ; max. resolution (IR) 1.3 cm^{-1} .

thyminato-N3) *cis*-diammineplatinum(II) moiety is evident from the solid state IR spectrum. There is, among other changes, a characteristic shift of the strong 1570 cm^{-1} band (with shoulder at 1540 cm^{-1}) of the Pt complex to 1520 cm^{-1} in the Pt_2Mn complex, very similar to the situation with a second platinum [2] or a proton [3] bound to one of the exocyclic oxygens of the thymine rings. In contrast, ionic binding through $\text{Ag}(\text{I})$ does not alter the band pattern on the bis(1-methylthyminato) platinum complex [3]. Again, it is believed that the shift of the 1570 cm^{-1} band to lower frequency reflects the reduction in double bond character of the coordinating keto group, and the considerable displacement of $\text{Mn}(\text{II})$ from the 1-methylthymine planes indeed supports such an interpretation. Because of the uncertainty concerning the donor atoms of $\text{Mn}(\text{II})$, the solid state vibrational spectra have been examined with regard to this question. The rationale behind this was the idea that different ways of metal binding should lead to differences in vibrations of the heterocyclic ligand. It has recently been shown that Raman spectroscopy permits a differentiation of heterocyclic tautomers in solution [9], in the solid state [10] and when coordinated to a metal [11, 12]. On the other hand, differences in respective modes of the types of coordination under consideration (N_3 , O_4 and/or N_3 , O_2)

might be smaller than those observed for monodentate metal binding to different sites.

Bis(1-methylthyminato-N3)cis-diammineplatinum(II) contains a single type of ligand binding of the heterocyclic ring to Pt (through N3). As a consequence, single bands are usually observed for IR and Raman modes which coincide within experimental error ($1-2\text{ cm}^{-1}$). This is shown in Fig. 3. for the $750-1250\text{ cm}^{-1}$ range, and is also true for the other areas of the spectra not shown. In few instances, bands are split, e.g. IR $1172, 1162\text{ cm}^{-1}$, Ra $1363, 1369\text{ cm}^{-1}$. These splittings may be due to factor group coupling or, less likely, due to coupling of the mutual *cis*-ligands, whereas Fermi resonance appears not to be responsible.

A comparison of IR and Raman frequencies of the Pt_2Mn compound with those of *cis*- $\text{Pt}(\text{NH}_3)_2\text{T}_2$ shows that there are several non coincident bands in the spectra of the heteronuclear complex, where in the parent compound coincident lines are observed. For example, the most intense Raman band, the ring-breathing mode, occurs in *cis*- $\text{Pt}(\text{NH}_3)_2\text{T}_2$ at 787 (Ra) and 786 cm^{-1} (IR), but at 800 (Ra) and 805 cm^{-1} (IR) in the Pt_2Mn compound. Another intense Raman mode absorbing at $1219, 1201\text{ cm}^{-1}$ in the Pt_2Mn compound, has its IR counterpart at 1210 cm^{-1} , whereas in *cis*- $\text{Pt}(\text{NH}_3)_2\text{T}_2$ these modes are observed at 1216 (Ra) and 1215 cm^{-1} (IR). The Raman band at 1432 cm^{-1} has its IR counterpart at 1420 cm^{-1} in the Pt_2Mn compound, compared to 1427 (Ra) and 1425 cm^{-1} (IR) in *cis*- $\text{Pt}(\text{NH}_3)_2\text{T}_2$. Thus vibrational spectroscopy suggests that there is a real centre of symmetry in the heteronuclear complex. Provided two different bridges were present, this would imply the two types to be present in 1:1 ratio, with equivalent bridges *trans* to each other. However, such a possibility seems to be very unlikely, since there is virtually no increase in the number of IR and Raman bands when going from *cis*- $\text{Pt}(\text{NH}_3)_2\text{T}_2$ to the Pt_2Mn complex.

The appearance of a new Raman band at 783 cm^{-1} in the spectrum of the Pt_2Mn compound merits some comment. Since this band occurs in the range of the very intense ring-breathing mode, it might be attributed to such a mode, hence support the existence of two different types of bridges. On the other hand, the low intensity of this band compared to that at 800 cm^{-1} rules against such a mode: Because of the required 1:1 ratio of two different kind of bridges, comparable intensities should be expected for the ring-breathing modes. With uracil tautomer complexes [11], as well as uracilato bridged complexes [13], for example, always com-

parable intensities of this mode for the various types of binding are observed. The origin of the weak 783 cm^{-1} band might be explained in a different way: with the Pt T Mn unit having C_1 symmetry only (the C_s symmetry of the Pt T unit is lost as a consequence of Mn not being coplanar with T and Pt), the original out-of-plane modes (A'') modes of the 1-methylthymine ligands which, under C_s symmetry, usually are too low in intensity to be observed, might be sufficiently activated to appear in the Raman spectrum. Coupling of modes of ligands related by a centre of symmetry should lead to doubling of bands ($A \rightarrow A_g + A_u$) with A_g being Raman active and A_u being IR active. Thus the weak 783 cm^{-1} Raman band could be the counterpart of one of the two very intense IR bands at 778 and 772 cm^{-1} . In conclusion, IR and Raman solid state spectra do not exhibit convincing evidence for the existence of more than a single type of 1-methylthyminato bridge in bis[bis(μ -1-methylthyminato) *cis*-diammineplatinum(II)] manganese(II) dichloride decahydrate. As outlined above, it is suggested that bridging of Pt and Mn through the 1-methylthyminato ligands occurs via N3 and O4. Work is in progress to further clarify this question.

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