Synthesis and Crystal Structure of a Novel Cyclic Trinuclear Platinum(II) Complex, $[Pt_3(\text{L-HMet})_3]\cdot H_2O$ (H_3Met = methionine)[†]

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Reaction of L-methionine hydrochloride $[H_4Met]Cl$ with 1 equivalent of $K_2[PtCl_4]$ under basic conditions (pH 12.36) in aqueous solution gave pale yellow crystals of $[Pt_3(\text{L-HMet})_3]\cdot H_2O$, as evidenced by X-ray crystallography: monoclinic, space group $P2_1$, $a = 8.396(2)$, $b = 8.331(2)$, $c = 16.872(2)$ Å, $\beta = 94.11(1)°$, $Z = 2$. The structure was refined to $R = R' = 0.075$ for 3791 reflections with $I > 3.00\sigma(I)$. It reveals a cyclic trinuclear platinum(II) complex with bridging amido nitrogens and an approximate three-fold axis of symmetry. Each Pt^{II} has roughly square-planar geometry with nitrogen, sulfur co-ordination from one methionine, and nitrogen, oxygen co-ordination from a second methionine.

Cisplatin, *cis*-$[Pt(NH_3)_2Cl_2]$, is one of the most widely used anticancer drugs, and this fact has led to intense interest in the reactions of platinum(II) with biologically relevant compounds. The reactions of Pt^{II} with one such compound, methionine (H_3Met), have been studied since 1962,[1] and the discovery of a platinum–methionine adduct in the urine of patients undergoing cisplatin therapy[2] has prompted additional studies of the reactions of Pt^{II} with methionine.

L-Methionine contains four atoms capable of metal binding: the amine nitrogen, the two carboxylate oxygens and the thioether sulfur. Generally, the binding of L-Met and its derivatives to Pt^{II} is reported to occur either in a monodentate manner through sulfur,[1,3] bidentate through nitrogen and sulfur,[1,4–6] or, at low pH ($\leqslant 0.5$), bidentate through oxygen and sulfur.[7] The reactions of L-Met with Pt^{II} in aqueous systems generate equilibrium mixtures containing, for example, as many as 10 different species[‡] in the reaction[6] of 2 equivalents of L-H_3Met with 1 equivalent of $[PtCl_4]^{2-}$. These studies were conducted over a pH range of 1.9–8.7. Interestingly, at pH 9, L-methionine *S*-oxide (L-MetO) binds Pt in a tetradentate bridging fashion through sulfur, oxygen, and a bridging amide.[8] The analogous binding of L-Met to Pt^{II} has not been reported.

Given the complexity of the aqueous solution chemistry of Pt^{II} and L-Met, perhaps it is not surprising that very few crystallographic studies of the system have been reported: $[Pt(\text{L-}H_3Met)Cl_2]$, $[Pt(\text{Gly-L-HMet})Cl]$, $[Pt(\text{L-}H_3MetO)Cl_2]$ and $[Pt_2(\text{L-HMetO})_2]$.[4,8,9]

We report herein the synthesis and crystal structure of a novel cyclic platinum trimer with bridging amides: $[Pt_3(\text{L-HMet})_3]\cdot H_2O$.

Experimental

Materials and Methods.—The compounds $[\text{L-}H_4Met]Cl$, NaOH and $K_2[PtCl_4]$ were obtained commercially and used without purification. All pH measurements were made using an Orion Research digital ionalyzer/501 and a pH combination (Ag–AgCl reference) electrode.

Synthesis.—$[Pt_3(\text{L-HMet})_3]\cdot H_2O$. A solution containing $K_2[PtCl_4]$ (0.1391 g, 0.335 mmol) and $[\text{L-}H_4Met]Cl$ (0.0501 g, 0.336 mmol) was prepared in deionized water (5.0 cm^3). It was stirred at room temperature for approximately 20 min and a yellow precipitate formed {presumably $[Pt(\text{L-}H_3Met)Cl_2]$}. The pH was then carefully adjusted with 5.0 mol dm^{-3} NaOH from around 2 to 12.36. The precipitate dissolved. The solution was reduced to half its volume by evaporation at 325 K, then covered with Parafilm and left undisturbed for 3 weeks when pale yellow crystals began to form.

Crystallography.—Crystal data. $C_{15}H_{29}N_3O_7Pt_3S_3$, $M = 1044.86$, monoclinic, space group $P2_1$ (no. 4), $a = 8.396(2)$, $b = 8.331(2)$, $c = 16.872(2)$ Å, $\beta = 94.11(1)°$, $U = 1177.1(3)$ Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections in the range $58.16 \leqslant 2\theta \leqslant 59.97°$, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 2.948$ g cm^{-3}, $F(000) = 956$. Pale yellow irregular crystals of dimensions $0.70 \times 0.50 \times 0.30$ mm, $\mu(\text{Mo-K}\alpha) = 180.20$ cm^{-1}.

Data collection and processing. Rigaku AFC7R diffractometer with a 12 kW rotating anode generator, ω–2θ mode with ω scan width $= 1.47 + 0.35 \tan\theta$, ω scan speed 16.0° min^{-1}, graphite-monochromated Mo-Kα radiation, 1.0 mm collimator; 4778 reflections measured ($4.8 \leqslant 2\theta \leqslant 65.0$, $+h$, $+k$, $\pm l$), 4520 unique [merging $R = 0.107$ after absorption correction (maximum, minimum transmission factors = 0.9898, 0.1929)], giving 3791 with $I > 3.00\sigma(I)$. A linear correction was applied for an increase (0.93%) in the intensities of the standards.

Structure analysis and refinement. Direct methods[10] expanded using Fourier techniques.[11] Full-matrix least-squares refinement[§] with 25 of the 31 non-hydrogen atoms anisotropic and hydrogens in calculated positions assigned a thermal parameter 1.20 times that of the atoms to which they are bonded. Final R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}\}$ values were both 0.075. The use of L-methionine determined the chirality of the molecule. This was corroborated

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[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. 1, xxv–xxx.

[‡] Three different chemical species with their different conformations (four for the first, three for the others): $[Pt(\text{L-}H_3Met\text{-}S,N)(\text{L-}H_4Met\text{-}S)Cl]^{2+}$, *cis*- and *trans*-$[Pt(\text{L-}H_2Met\text{-}S,N)_2]$.

[§] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$ and $\sigma^2(F_o^2) = S^2(C + R^2B) + (pF_o^2)^2/L_p^2$ with S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, L_p = Lorentz-polarization factor, and p = factor to downweight the intense reflections = 0.007.

by refinement of the inverted structure (corresponding to D-methionine, $R = 0.077$). Neutral atom scattering factors were taken from Cromer and Waber.[12] Anomalous dispersion effects were included in F_c;[13] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[14] The values for the mass attenuation coefficients were those of Creagh and Hubbell.[15] All calculations were performed using the TEXSAN[16] crystallographic software package. The atomic positions are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

An ORTEP[17] diagram of the complex with a partial atom labelling scheme is shown in Fig. 1. Some relevant bond distances and angles are contained in Table 2 and are compared to literature values in Tables 3 and 4. The complex consists of three crystallographically independent but highly similar platinum(II) centres related by an approximate three-fold axis. Each Pt atom binds to a carboxylate oxygen and μ-amido nitrogen of one L-HMet^{2-}, and the sulfur and μ-amido nitrogen of another L-HMet^{2-} in a roughly square-planar arrangement. In each case the atom showing the largest deviation from the best least-squares plane through the platinum and its four ligating atoms is the amido nitrogen atom which participates in the N,O chelate ring bound to that platinum. Thus, N(11) shows the largest deviation from the plane involving Pt(1). The Pt–O distances are typical (see Table 3) with an average of 2.03(1) Å which compares well with that found for the $[Pt_2(\text{L-HMetO})_2]$ complex and with that found in the second-generation platinum drug carboplatin, *cis*-$[Pt(NH_3)_2(\text{cbdca})]$ (H_2cbdca = cyclobutane-1,1-dicarboxylic acid).

Both the Pt–N and Pt–S distances differ from those reported and expected for other comparable compounds. We observe shorter Pt–N and longer Pt–S distances in $[Pt_3(\text{L-HMet})_3]$ than those in $[Pt_2(\text{L-HMetO})_2]$. The differences are attributable to two different effects which work in concert. The first is the strong basicity of the μ-amido nitrogen. Typically Pt–NH_2R distances are around 2.05(2) Å (see Table 3), while the average distance in this complex is 2.02(1) Å. Other μ-amido groups have Pt–N distances of around 2.11(2) Å, but these all involve NH_2^-. The only really appropriate comparison is to $[Pt_2(\text{L-HMetO})_2]$ which has an average distance of 2.041(3) Å. The second effect is that thioethers are relatively weaker bases than are the corresponding sulfoxides, and a weaker base leads to a longer Pt–S distance. For example, the Pd–S distance in $[Pd\{\text{L-}H_3\text{Cys(Me)}\}Cl_2]$[34] [$H_3$Cys(Me) = *S*-methylcysteine] is 2.246 Å, while it is 2.200 Å in $[Pd\{\text{L-}H_3\text{CysO(Me)}\}Cl_2]$[35] [$H_3$CysO(Me) = *S*-methylcysteine *S*-oxide]. Similar effects are seen for platinum complexes, see Table 3, with the Pt–S bond typically 0.05 Å longer than the Pt–SO bond. Thus, if all else is equal, based upon the $[Pt_2(\text{L-HMetO})_2]$ distance of 2.202 Å, we would predict a Pt–S distance of 2.25 Å in $[Pt_3(\text{L-HMet})_3]$, but the observed distance is longer at 2.267(5) Å. This longer distance can be explained by considering the stronger basicity of the μ-amido nitrogen relative to the thioether sulfur. From the bond distances seen in this compound, we suggest that the

Table 1 Fractional atomic coordinates for $[Pt_3(\text{L-HMet})_3]\cdot H_2O$

Atom	*x*	*y*	*z*
Pt(1)	−0.167 6(1)	−0.241 2	−0.243 05(7)
Pt(2)	−0.466 5(1)	−0.060 7(2)	−0.167 30(7)
Pt(3)	−0.332 0(1)	0.071 6(2)	−0.335 03(7)
S(11)	−0.561(1)	−0.289(1)	−0.113 8(5)
S(21)	−0.552(1)	0.162(1)	−0.406 9(7)
S(31)	−0.101 0(8)	−0.368(1)	−0.354 4(5)
O(3)	−0.932(3)	−0.313(3)	−0.877(2)
O(11)	−0.210(3)	−0.447(3)	−0.183(1)
O(12)	−0.232(3)	−0.545(3)	−0.066(1)
O(21)	−0.684(3)	0.044(3)	−0.187(1)
O(22)	−0.799(3)	0.277(4)	−0.203(2)
O(31)	−0.244(3)	−0.002(3)	−0.437(1)
O(32)	−0.027(4)	−0.074(4)	−0.496(2)
N(11)	−0.245(3)	−0.141(3)	−0.147(1)
N(21)	−0.413(3)	0.145(3)	−0.233(2)
N(31)	−0.120(3)	−0.026(3)	−0.290(1)
C(11)	−0.226(4)	−0.432(5)	−0.112(2)
C(12)	−0.204(4)	−0.261(4)	−0.077(2)
C(13)	−0.308(4)	−0.234(5)	−0.006(2)
C(14)	−0.486(5)	−0.294(5)	−0.016(2)
C(15)	−0.772(5)	−0.278(6)	−0.102(3)
C(21)	−0.683(4)	0.189(5)	−0.205(2)
C(22)	−0.523(4)	0.266(5)	−0.214(2)
C(23)	−0.545(4)	0.394(5)	−0.287(2)
C(24)	−0.623(4)	0.335(6)	−0.356(2)
C(25)	−0.472(6)	0.25(1)	−0.490(3)
C(31)	−0.096(5)	−0.027(6)	−0.437(3)
C(32)	−0.009(4)	−0.016(4)	−0.353(2)
C(33)	0.134(4)	−0.137(4)	−0.341(2)
C(34)	0.096(5)	−0.305(5)	−0.367(3)
C(35)	−0.074(4)	−0.577(4)	−0.334(2)

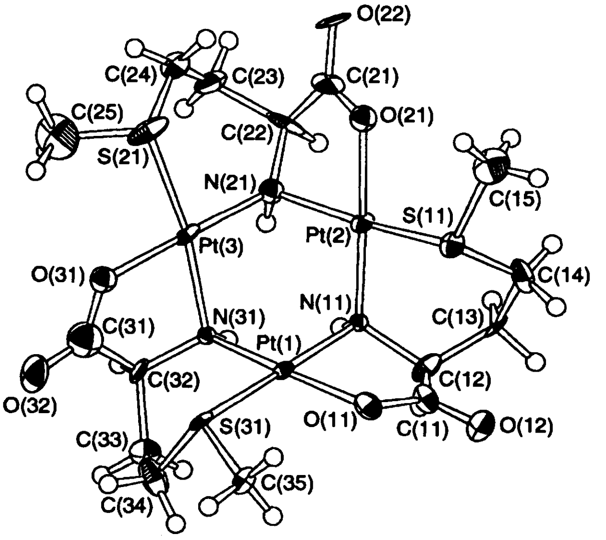

Fig. 1 An ORTEP diagram of $[Pt_3(\text{L-HMet})_3]$ with the non-hydrogen-atom labelling scheme. Ellipsoids are at the 50% probability level

Table 2 Intramolecular distances (Å) involving the non-hydrogen atoms

Pt(1)–S(31)	2.262(8)	O(11)–C(11)	1.22(4)
Pt(1)–O(11)	2.04(2)	O(12)–C(11)	1.23(4)
Pt(1)–N(11)	1.98(2)	O(21)–C(21)	1.24(5)
Pt(1)–N(31)	2.01(2)	O(22)–C(21)	1.23(4)
Pt(2)–S(11)	2.273(8)	O(31)–C(31)	1.27(4)
Pt(2)–O(21)	2.03(2)	O(32)–C(31)	1.24(4)
Pt(2)–N(11)	1.99(2)	N(11)–C(12)	1.56(4)
Pt(2)–N(21)	2.11(3)	N(21)–C(22)	1.42(4)
Pt(3)–S(21)	2.27(1)	N(31)–C(32)	1.45(3)
Pt(3)–O(31)	2.01(2)	C(11)–C(12)	1.54(5)
Pt(3)–N(21)	1.98(3)	C(12)–C(13)	1.55(4)
Pt(3)–N(31)	2.05(2)	C(13)–C(14)	1.57(5)
S(11)–C(14)	1.73(4)	C(21)–C(22)	1.51(5)
S(11)–C(15)	1.81(4)	C(22)–C(23)	1.63(6)
S(21)–C(24)	1.80(4)	C(23)–C(24)	1.38(5)
S(21)–C(25)	1.75(6)	C(31)–C(32)	1.56(6)
S(31)–C(34)	1.76(4)	C(32)–C(33)	1.57(4)
S(31)–C(35)	1.78(3)	C(33)–C(34)	1.49(5)

Estimated standard deviations in the least significant figure are given in parentheses.

Table 3 Selected bond distance (Å) and angle (°) comparisons

Compound	Pt–S	Pt–O	Pt–N	Pt–N–Pt	Ref.
$[Pt_3(L\text{-}HMet)_3]\cdot H_2O$ (av.)	2.267(5)	2.03(1)	2.02(1)	108(1)	This work
$[Pt_2(L\text{-}HMetO)_2]$	2.197(2)	2.045(7)	2.040(7)	88.9(3)	8
			2.046(7)	89.1(3)	
	2.208(2)	2.027(7)	2.040(7)		
			2.038(8)		
$[Pt(NH_3)_2(cbdca)]$		2.029(9)	2.010(8)		18
$[Pt(L\text{-}H_3MetO)Cl_2]$	2.198(2)		2.063(7)		9
$[Pt\{L\text{-}H_3CysO(Me)\}Cl_2]$	2.182(3)		2.046(12)		19
$[Pt(L\text{-}H_3Met)Cl_2]$	2.246(2)		2.047(8)		4
	2.247(2)		2.029(8)		
$[Pt(DL\text{-}H_3Eth)Cl_2]$	2.244(2)		2.042(6)		20
$[Pt(cbdca)(L^1)(dmso)]$	2.230(8)	1.98(2)	2.02(2)		21
			2.07(2)		
	2.220(10)	2.02(2)	2.05(2)		
			2.10(3)		
	2.207(10)	2.05(2)	2.02(2)		
			2.03(2)		
	2.207(8)	2.05(2)	2.05(2)		
			2.06(2)		
$[Pt_2(PMePh_2)_2(POPh_2)_2(NH_2)_2]$			2.107(13)	93.5(5)	22
			2.127(14)	94.1(5)	
			2.109(11)		
			2.112(13)		
$[Pt_2(PPh_3)_2Me_2(NH_2)_2]$			2.13(1)	95.2(4)	23
			2.14(1)	95.1(3)	
			2.08(1)		
			2.09(1)		
$[Pt_2(PMe_2Ph)_4(NH_2)_2]^{2+}$			2.091(5)	97.4(2)	24
			2.081(4)		
$[\{PtCl(L^2)\}_2]$			2.07(2)	91.4(6)	25
			2.10(2)		
$[PtCl(SMe_2)L^3]$	2.266(3)				26
$[PtCl_2(py)(dmso)]$	2.224(2)				27
	2.225(3)				
$[Pt(Gly\text{-}L\text{-}HMet)Cl]$	2.258(2)		2.004(4)		4
			2.046(5)*		

L^1 = *trans*-(−)-Cyclohexane-1,2-diamine; L^2 = *o*-isopropenylphenyl(methyl)amide; L^3 = chloro(2-pyridylcarbonyl)methyl; py = pyridine.
* The 2.004 Å distance refers to the amide N to Pt bond, the 2.046 Å to the amine N to Pt bond.

Table 4 Selected bond distance (Å) comparisons

Compound	C_c–O(R)	C_c–O	C_c–C_α	C_α–N	C_α–C_β	C_β–C_γ	C_γ–S	S–C_m	Ref.
$[Pt_3(L\text{-}HMet)_3]\cdot H_2O$ (avg.)	1.24(3)	1.23(2)	1.54(3)	1.48(2)	1.58(3)	1.48(3)	1.76(2)	1.78(3)	This work
S,*N* Bonded methionine complexes									
$[Pt(L\text{-}H_3Met)Cl_2]$	1.285(13)	1.205(12)	1.491(12)	1.478(12)	1.507(11)	1.542(11)	1.785(11)	1.811(9)	4
	1.310(13)	1.225(12)	1.514(13)	1.469(12)	1.526(12)	1.521(16)	1.814(13)	1.819(12)	
$[Pt(DL\text{-}H_3Eth)Cl_2]$	1.31(1)	1.22(1)	1.51(1)	1.50(1)	1.48(1)	1.55(1)	1.802(7)	1.85(1)	20
$[Pt(Gly\text{-}L\text{-}HMet)Cl]$	1.335(8)	1.192(8)	1.509(8)	1.465(6)	1.517(8)	1.520(10)	1.834(6)	1.821(7)	4
$[Pt(L\text{-}H_3MetO)Cl_2]$	1.328(12)	1.235(12)	1.474(14)	1.485(11)	1.534(13)	1.529(13)	1.781(9)	1.778(11)	9
$[Pd(DL\text{-}H_3Met)Cl_2]$	1.295(23)	1.205(21)	1.536(22)	1.472(23)	1.506(23)	1.493(22)	1.827(16)	1.800(21)	28
$[Pd(DL\text{-}H_3Met)I_2]$	1.32(2)	1.17(2)	1.54(2)	1.48(2)	1.50(2)	1.55(2)	1.80(2)	1.77(2)	29
$[Pd(L\text{-}H_3Met)Cl_2]$	1.279(8)	1.237(8)	1.545(8)	1.502(9)	1.502(9)	1.550(9)	1.829(6)	1.813(7)	30
$[Ru(Me\text{-}DL\text{-}H_2Met)Cl_2(nbd)]$	1.28(2)	1.18(2)	1.54(2)	1.44(2)	1.51(2)	1.47(2)	1.80(2)	1.84(2)	31
$[Ru(Me\text{-}L\text{-}H_2Met)_2(PPh_3)Cl]Cl$	1.32(3)	1.16(4)	1.55(4)	1.47(3)	1.53(4)	1.47(4)	1.83(2)	1.80(4)	32
	1.32(4)	1.17(4)	1.56(3)	1.48(3)	1.54(4)	1.47(4)	1.83(2)	1.80(3)	
$[Ru(Et\text{-}L\text{-}H_2Met)(PPh_3)Cl_3]$	1.33(1)	1.18(1)	1.51(1)	1.48(1)	1.52(1)	1.52(1)	1.785(9)	1.819(9)	32
	1.31(1)	1.18(1)	1.51(1)	1.47(1)	1.53(1)	1.52(1)	1.790(8)	1.78(1)	
S,*N*,*O*-Bonded methionine complexes									
$[Pt_2(L\text{-}HMetO)_2]$	1.288(12)	1.220(11)	1.525(13)	1.467(11)	1.526(14)	1.528(15)	1.785(10)	1.753(9)	8
	1.280(3)	1.238(12)	1.540(12)	1.478(11)	1.512(14)	1.510(15)	1.812(11)	1.767(10)	
$[Cu_2L^4Br_2]$	1.32(1)	1.20(1)	1.51(1)	1.48(1)	1.56(2)	1.51(2)	1.83(1)	1.79(1)	33
$[Ru(DL\text{-}H_2Met)Cl(nbd)]$	1.275(9)	1.24(1)	1.55(1)	1.49(1)	1.58(1)	1.54(1)	1.84(1)	1.81(1)	31
	1.25(1)	1.24(1)	1.51(1)	1.49(1)	1.55(2)	1.57(1)	1.83(1)	1.80(1)	

L^4 = *N*,*N*′-(1,2-Dithioxoethane-1,2-diyl)bis(*O*-methyl methionine).

μ-amido nitrogen is properly placed between thioethers and sulfoxides in the *trans*-influence series. In $[Pt_3(L\text{-}HMet)_3]$ the stronger *trans*-influencing μ-amido nitrogen lengthens the Pt–S bond, while in $[Pt_2(L\text{-}HMetO)_2]$ the stronger *trans*-influencing sulfoxide lengthens the Pt–N bond.

The angle at nitrogen is the largest in $[Pt_3(L\text{-}HMet)_3]$

[108(1)°] as compared to other bridging amido complexes (see Table 3). Similarly, the N–Pt–N angles in [Pt_3(L-HMet)$_3$] are also the largest. Both of these facts suggest that there is relatively little strain in [Pt_3(L-HMet)$_3$]; the angles are very close to ideal values.

In addition to the chair-shaped (Pt–N)$_3$ ring, the structure of [Pt_3(L-HMet)$_3$] contains three six- and three five-membered chelate rings. These six-membered chelate rings all exhibit a twisted-boat conformation, while the five-membered rings are all twisted. It is interesting that in all of the structures known to us of the form $ML_x(MetX\text{-}S,N)_y$ (MetX is methionine or a methionine derivative, $x = 2$–4, $y = 1$ or 2), [Pt(L-H_3Met)Cl_2], [Pt(DL-H_3Eth)Cl_2] (H_3Eth = *S*-ethylhomocysteine), [Pt(L-H_3MetO)Cl_2], [Pd(DL-H_3Met)Cl_2], [Pd(DL-H_3Met)I_2], [Pd-(L-H_3Met)Cl_2], [Ru(Me-DL-H_2Met)Cl_2(nbd)] (Me-H_2Met = *O*-methyl methionine, nbd = norbornadiene), [Ru(Me-L-H_2-Met)$_2$(PPh_3)Cl]Cl and [Ru(Et-L-H_2Met)(PPh_3)Cl_3], the six-membered ring adopts a chair conformation. There are four cases with additional bonds from the MetX ligand: [Pt_2(L-HMetO)$_2$], [Pt(Gly-L-HMet)Cl], [$Cu_2L^4Br_2$] and [Ru(DL-H_2Met)Cl(nbd)]. In the last two cases the MetX ligand co-ordinates facially and the six-membered ring adopts a chair conformation. In the two platinum(II) complexes, which may be viewed as having a meridionally co-ordinated ligand {even though the ligand actually bridges in the [Pt_2(L-HMetO)$_2$] case}, the MetX ligand has a twisted-boat conformation, as observed in [Pt_3(L-HMet)$_3$]. Examination of a space-filling model for [Pt_3(L-HMet)$_3$] suggests that the twisted-boat conformation is the result of steric constraints imposed by the 'extended' conformation of the amino acid and the positioning of the non-co-ordinated carboxyl oxygen. The five-membered ring conformations are somewhat unusual. Typically in an isolated five-membered ring, such as that found in ethylenediamine complexes, the ring distorts in such a way to give an approximate two-fold axis which bisects the C–C bond and contains the metal centre.[36] Thus one carbon lies above and the other below the plane defined by the metal centre and two donor atoms. Instead, in [Pt_3(L-HMet)$_3$], a reasonably good plane is defined by the Pt, O, carboxylate carbon, and α-carbon with the nitrogen displaced from this plane toward the next platinum atom. Perhaps this is best described as an envelope conformation.

Each L-$HMet^{2-}$ makes four bonds to two different platinum(II) centres, simultaneously chelating and bridging. The distances within the L-$HMet^{2-}$ ligand are collected in Table 2 and compared with those of relevant compounds in Table 4. They show the patterns expected for metal complexes.

Additionally, there is a single water molecule in the asymmetric unit. It apparently participates in three hydrogen bonds with three different Pt_3(L-HMet)$_3$ units: two bonds to two of the L-$HMet^{2-}$ non-bonded carboxylate oxygen atoms O(12) and O(22) of different units (2.815 and 2.796 Å respectively), and one bond to one of the amido nitrogens N(11) (3.127 Å). The oxygen–oxygen distances are typical, and the nitrogen–oxygen distance is slightly longer than the average [3.04(13) Å for amine–oxygen],[37] but not significantly so. This hydrogen-bonding network helps to hold the crystal together.

The last detail of the structure to consider is the Pt $\cdots$ Pt separation. In [Pt_3(L-HMet)$_3$] the average distance is 3.29(2) Å. This is considerably longer than the 2.8605(6) Å found[8] in [Pt_2(L-HMetO)$_2$]. However, the distance in our compound is comparable to the observed separation of 3.285(5) Å in the μ-hydroxo species[38] [{$Pt(NH_3)_2$}$_3$(OH)$_3$]$_2$[SO_4]$_3$·6H_2O, and shorter than those observed[39] in other μ-hydroxo species, [{$Pt(NH_3)_2$}$_3$(OH)$_3$][NO_3]$_3$ [3.44(9) Å] and [$Pt_3(\mu_3\text{-}OH)(\mu\text{-}OPPh_2)_3(PMePh_2)_3$][$BF_4$]$_2$·$H_2O$·$CH_2Cl_2$ [3.6(1) Å]. Recently, a series of Raman studies was reported[40] which correlated values of Pt–Pt separations to values of ν(Pt_2) and suggested that weak Pt $\cdots$ Pt interactions occur at separations up to 4.22 Å. Of relevance to [Pt_3(L-HMet)$_3$], the authors report a ν(Pt_2) of 43 cm^{-1} for [(Me)ClPt(μ-Cl){μ-$PPh_2(C_5H_4N)$}PtMe(dmso)]·dmso (dmso = dimethyl sulfoxide) with a separation of 3.308 Å and suggested a Pt $\cdots$ Pt interaction, which, in turn, would suggest a similar interaction in our compound. We are planning Raman studies on [Pt_3(L-HMet)$_3$]·H_2O to determine whether such a Pt $\cdots$ Pt interaction is present.

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