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Crystal structure, ^{195}Pt and ^{1}H–^{13}C COSY NMR and FAB mass spectroscopic studies of amidate-bridged binuclear platinum(II) complex, head-to-tail $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$

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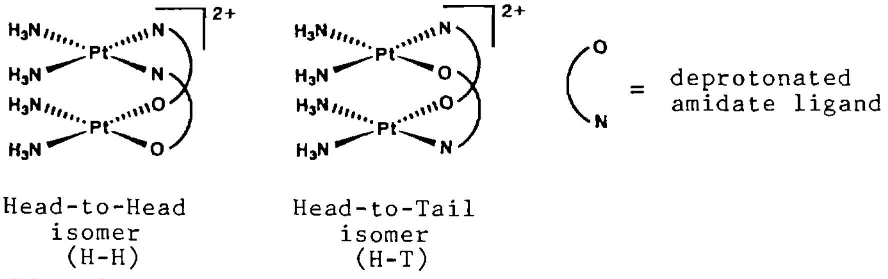
Abstract

The synthesis and crystal structure of the α-pyrrolidonate-bridged binuclear complex $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$ are reported. The complex is prepared by the reaction of $Pt(bpy)Cl_2$ with α-pyrrolidone in H_2O. The complex crystallizes in monoclinic, space group $C2/c$, $a=29.992(4)$, $b=12.430(1)$, $c=18.842(3)$ Å, $\beta=112.191(8)°$, $Z=8$, $V=6504(2)$ Å^3. The structure was refined with 4033 independent reflections to $R=0.079$. The complex is a head-to-tail binuclear structure, bridged by nitrogen and oxygen atoms of the two α-pyrrolidonate ligands. No isomerization to a head-to-head isomer was observed in acetonitrile which was confirmed with ^{1}H–^{13}C COSY NMR spectrometry. Cyclic voltammetry exhibited an irreversible wave at $E_{pa}=1.19$ and $E_{pc}=0.84$ V versus SCE in acetonitrile. FAB mass spectroscopy showed major peaks corresponding to the molecular formula, and proved the applicability of the method for the determination of the molecular weights of this sort of cationic complex.

Introduction

Several binuclear Pt(II) complexes with two amidate bridging ligands in *cis* position of the type $[Pt_2A_4L_2]^{2+}$ (A is amine ligand and L is deprotonated amidate ligand) (Scheme 1) have been reported and the dependence of the redox potentials and the oxidizability to binuclear Pt(III) complexes or tetranuclear platinum blues on the coordinated amine and amidate ligands have been discussed [1–3]. All the complexes so far reported are prepared with DNA bases or lactams such as 1-methylthymine (1-MeT) [4, 5], 1-methyluracil (1-MeU) [6], α-pyridone [7–9], α-pyrrolidone [10] or 1-methylhydantoin [11] as the bridging ligands, and mostly with NH_3 or en (ethylenediamine) as the amine ligands. In this respect, bipyridine (bpy) as the amine ligand is expected to exhibit different characteristics, compared to NH_3 or en complexes, due to the extended π* orbital of the ligand capable of accommodating electron back-donation form the Pt(II) atoms. Lippert and co-workers reported that $[Pt(II)_2(bpy)_2(1\text{-MeU})_2](NO_3)_2 \cdot 3H_2O$ exhibits Pt(2.0)/Pt(3.0) redox potential at 0.932 V versus



Scheme 1.

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Ag/AgCl, which is about 0.28 V more positive than those of $[Pt_2A_2(1\text{-}MeU)_2]^{2+}$ (A = NH_3, en/2) [1]. This fact suggests that the backdonation from the Pt(II) atoms to bpy and the resulting lower electron density at the Pt atom renders the compound more resistant to oxidation and therefore the redox potential shifts to a more positive value.

In the present study, we report the synthesis of head-to-tail (H-T) $[Pt(II)_2(bpy)_2(\alpha\text{-pyrrolidonato})_2]^{2+}$ and compare the oxidizability of the compound to that of the previously reported head-to-head (H-H) α-pyrrolidonate-bridged Pt(II) binuclear complex $[Pt_2(NH_3)_4(\alpha\text{-pyrrolidonato})_2]^{2+}$. We also report here the details of the crystal structure of H-T $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$. The structure is especially noted with regard to the comparison of the *trans* effect so far observed in Pt–N (NH_3 or en) distances *trans* to the amidate-nitrogen atoms. In H-H $[Pt_2(NH_3)_4(\alpha\text{-pyrrolidonato})_2]^{2+}$ the amidate-nitrogen atom shows stronger *trans* influence compared to the amidate-oxygen atom and therefore the Pt–N(NH_3) distance *trans* to the amidate-nitrogen atom is longer than that *trans* to the amidate-oxygen atom [10]. In addition to the structural study, FAB mass spectroscopy is described in the present paper to demonstrate how the method is effective and can be useful for the determination of the molecular weight of this sort of complex. ^{195}Pt and ^{1}H–^{13}C COSY NMR spectra are also presented to examine whether H-T to H-H isomerization takes place in solution. Such isomerization has been reported for analogous amidate-bridged Pt(II) binuclear complexes with NH_3 or en as the amine ligands and with α-pyridonate or α-pyrrolidonate as the amidate ligands [10, 12, 13].

Experimental

Preparation of the compound

$[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$ was prepared by reacting the suspension of 0.42 g of $Pt(bpy)Cl_2$ with 0.34 g of $AgNO_3$ and 600 μl of α-pyrrolidone in 20 ml H_2O at room temperature with vigorous stirring for 30 min under a light shielding. The reaction was further continued at 80 °C for 6 h. After the solution was cooled at first to room temperature and then to 5 °C, AgCl and the unreacted yellow precipitate were removed. To the red filtrate 2 g of $NaClO_4$ were added, which produced a violet precipitate. The precipitate was dissolved in acetonitrile and the saturated solution was left in a dark silical gel desiccator. After a few days reddish brown plate crystals appeared (yield 42%). *Anal.* Found: C, 31.12; H, 2.75; N, 7.97. Calc. for $Pt_2Cl_2C_{28}H_{28}N_6O_{10}$: C, 31.44; H, 2.64; N, 7.86%.

Spectroscopic measurements

UV–Vis spectra were recorded on a Shimadzu UV-260 spectrophotometer. Cyclic voltammetry was performed with a three electrode system consisting of a graphite plate working electrode, a platinum wire counter electrode and SCE as a reference electrode which was shielded from the sample solution by a Luggin tube. The potentiostat used was FUSO 3A. FAB mass spectroscopy was carried out on a JEOL JMS-HX110 spectrometer. The sample was applied as a nitrobenzylalcohol solution. The ^{195}Pt NMR spectrum was acquired on a JEOL FX90A spectrometer. The measurement was performed at 19.21 MHz. Since the 90° pulse was 16μs, 22.5° pulse (4 μs) was adopted for the accumulation. The Pt chemical shift is expressed as referenced to H_2PtCl_6 in D_2O. The ^{1}H–^{13}C COSY NMR spectrum was acquired on a Bruker AC200P at 50.3 MHz. An acetonitrile-d_3 solution was used for measurements at 25 °C. Chemical shift data are reported relative to TMS, which was set in a sealed coaxial capillary tube in a 5 mm sample tube.

X-ray crystallography

Unit cell parameters of the complex were obtained from a least-squares fit of 20 reflections in the range of $20 < 2\theta < 25°$ measured on a Rigaku AFC-5R four-circle diffractometer by using graphite-monochromated Mo Kα radiation ($\lambda = 0.71068$ Å). A crystal of approximate dimensions of 0.15 × 0.15 × 0.2 mm was used for measurement and the unit cell dimensions and the space group were: monoclinic, $C2/c$, $a = 29.992(4)$, $b = 12.430(1)$, $c = 18.842(3)$ Å, $\beta = 112.191(8)°$, $Z = 8$, $V = 6504(2)$ Å^3, formula weight = 1069.7, $D_{calc} = 2.18$ g cm^{-3}. The intensities were collected at room temperature with an ω–2θ scan in the range $3 < 2\theta < 55°$, of which 4033 independent reflections with $F_o > 4\sigma(F_o)$ were used for calculation. The intensities were corrected for Lorentz, polarization and absorption.

The coordinates of the two platinum atoms were deduced from a direct method (MULTAN) and a series of block-diagonal least-squares refinements followed by Fourier syntheses revealed all the remaining atoms except hydrogen atoms. The structure was finally refined with anisotropic temperature factors for all the non-hydrogen atoms and with isotropic ones for the hydrogen atoms to the final discrepancy index of $R = 0.079$ and $R_w = 0.082$, where $R = \Sigma\,||F_o| - |F_c||/\Sigma\,|F_o|$ and $R_w = [\Sigma w_i(|F_o| - |F_c|)^2/\Sigma w_i|F_o|^2]^{1/2}$ $(w_i = 1/\sigma^2(F_o))$. Atomic scattering factors and anomalous dispersion corrections were taken from ref. 14. All the calculations were performed with the program system UNICS-III [15] and ORTEP [16]. Absorption correction was made by following the method of North *et al.* [17]. The final positional and thermal parameters for non-hydrogen

TABLE 1. Positional and thermal parameters for [Pt$_2$(bpy)$_2$(α-pyrrolidonato)$_2$](ClO$_4$)$_2$

Atom	x/a	y/b	z/c
Pt(1)	0.05933(3)	0.12546(6)	0.33428(5)
Pt(2)	0.13841(3)	0.14674(6)	0.48092(5)
N(11)	0.076(1)	0.236(1)	0.272(1)
C(11)	0.102(1)	0.202(2)	0.233(1)
C(12)	0.121(1)	0.271(2)	0.189(2)
C(13)	0.110(1)	0.380(2)	0.189(2)
C(14)	0.082(1)	0.419(2)	0.229(1)
C(15)	0.064(1)	0.344(2)	0.269(1)
N(21)	0.094(1)	0.034(1)	0.284(1)
C(21)	0.112(1)	0.083(2)	0.239(1)
C(22)	0.139(1)	0.037(2)	0.203(1)
C(23)	0.147(1)	−0.075(2)	0.217(1)
C(24)	0.127(1)	−0.133(2)	0.265(2)
C(25)	0.100(1)	−0.076(2)	0.298(1)
N(31)	0.176(1)	0.244(1)	0.443(1)
C(31)	0.208(1)	0.193(2)	0.416(1)
C(32)	0.233(1)	0.250(2)	0.380(1)
C(33)	0.226(1)	0.366(2)	0.371(1)
C(34)	0.193(1)	0.412(2)	0.394(1)
C(35)	0.170(1)	0.352(2)	0.431(1)
N(41)	0.184(1)	0.039(1)	0.465(1)
C(41)	0.211(1)	0.075(2)	0.426(1)
C(42)	0.240(1)	0.010(2)	0.405(1)
C(43)	0.241(1)	−0.101(2)	0.422(2)
C(44)	0.212(1)	−0.139(2)	0.460(2)
C(45)	0.183(1)	−0.071(2)	0.483(1)
O(51)	0.026(1)	0.232(1)	0.379(1)
N(51)	0.092(1)	0.257(1)	0.493(1)
C(51)	0.051(1)	0.274(1)	0.445(1)
C(52)	0.021(1)	0.363(2)	0.470(1)
C(53)	0.060(1)	0.389(2)	0.554(2)
C(54)	0.108(1)	0.325(2)	0.563(1)
O(61)	0.104(1)	0.035(1)	0.517(1)
N(61)	0.045(1)	0.007(1)	0.398(1)
C(61)	0.066(1)	−0.010(1)	0.469(1)
C(62)	0.044(1)	−0.103(2)	0.499(1)
C(63)	0.003(1)	−0.138(2)	0.427(1)
C(64)	0.003(1)	−0.061(2)	0.363(1)
Cl(1)	0.2710(3)	0.1461(5)	0.2158(4)
Cl(2)	0.3989(3)	0.1352(5)	0.0596(5)
O1(1)	0.293(1)	0.149(2)	0.167(2)
O1(2)	0.271(1)	0.240(2)	0.247(2)
O1(3)	0.269(1)	0.060(2)	0.261(2)
O1(4)	0.232(1)	0.132(3)	0.156(2)
O2(1)	0.423(1)	0.142(2)	0.007(2)
O2(2)	0.399(1)	0.233(2)	0.091(2)
O2(3)	0.359(1)	0.086(3)	0.033(3)
O2(4)	0.431(1)	0.080(3)	0.110(2)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Pt(1)	0.00130(1)	0.00564(5)	0.00274(3)	0.00003(2)	0.00079(2)	0.00010(4)
Pt(2)	0.00110(1)	0.00623(6)	0.00316(3)	0.00038(2)	0.00071(2)	0.00040(4)
N(11)	0.0011(3)	0.0096(15)	0.0023(7)	0.0000(5)	0.0005(3)	−0.0012(8)
C(11)	0.0019(4)	0.0098(19)	0.0019(8)	0.0007(7)	0.0001(5)	0.0011(10)
C(12)	0.0024(6)	0.0155(29)	0.0051(14)	−0.0010(10)	0.0012(7)	0.0042(16)
C(13)	0.0028(6)	0.0158(30)	0.0044(12)	−0.0016(11)	0.0011(7)	0.0029(15)
C(14)	0.0032(7)	0.0131(26)	0.0038(12)	−0.0019(10)	0.0007(7)	0.0028(14)
C(15)	0.0028(6)	0.0079(19)	0.0039(11)	0.0003(8)	−0.0006(6)	0.0011(11)
N(21)	0.0017(3)	0.0098(15)	0.0022(7)	−0.0004(5)	0.0013(4)	−0.0011(8)
C(21)	0.0010(3)	0.0118(20)	0.0021(8)	−0.0007(6)	0.0007(4)	0.0002(10)

(continued)

TABLE 1. (*continued*)

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(22)	0.0021(5)	0.0169(28)	0.0022(9)	0.0009(9)	0.0010(5)	−0.0007(13)
C(23)	0.0017(5)	0.0188(30)	0.0035(11)	0.0018(9)	0.0013(6)	0.0001(15)
C(24)	0.0024(6)	0.0119(25)	0.0047(12)	0.0009(9)	0.0009(6)	0.0010(14)
C(25)	0.0016(4)	0.0075(17)	0.0036(10)	0.0007(6)	0.0006(5)	−0.0010(10)
N(31)	0.0006(2)	0.0080(13)	0.0032(7)	−0.0005(4)	0.0001(3)	−0.0012(7)
C(31)	0.0011(3)	0.0091(17)	0.0022(8)	0.0003(6)	−0.0003(4)	−0.0014(9)
C(32)	0.0010(4)	0.0119(22)	0.0042(11)	−0.0009(7)	0.0005(5)	0.0006(12)
C(33)	0.0023(5)	0.0149(27)	0.0031(10)	−0.0004(9)	0.0015(6)	0.0006(13)
C(34)	0.0016(4)	0.0082(18)	0.0050(12)	−0.0003(7)	0.0007(5)	0.0007(11)
C(35)	0.0013(4)	0.0068(16)	0.0049(11)	−0.0010(6)	0.0006(5)	−0.0008(10)
N(41)	0.0011(3)	0.0085(14)	0.0031(8)	0.0003(5)	0.0002(4)	−0.0001(8)
C(41)	0.0013(4)	0.0080(17)	0.0031(9)	0.0007(6)	0.0009(4)	0.0003(9)
C(42)	0.0017(5)	0.0114(21)	0.0035(10)	0.0005(8)	0.0009(5)	−0.0024(12)
C(43)	0.0027(6)	0.0101(22)	0.0051(13)	0.0008(7)	0.0017(7)	0.0013(13)
C(44)	0.0017(5)	0.0112(23)	0.0068(15)	0.0009(8)	0.0007(6)	−0.0026(15)
C(45)	0.0019(5)	0.0096(20)	0.0041(11)	0.0015(8)	−0.00005(55)	0.0010(12)
O(51)	0.0008(2)	0.0079(11)	0.0033(6)	0.0008(4)	0.0007(3)	−0.0002(6)
N(51)	0.0012(3)	0.0060(12)	0.0026(7)	0.0008(4)	0.0003(3)	−0.0000(7)
C(51)	0.0013(4)	0.0060(14)	0.0038(10)	−0.0003(6)	0.0011(5)	−0.0005(9)
C(52)	0.0018(4)	0.0073(17)	0.0057(12)	0.0001(7)	0.0022(6)	−0.0024(11)
C(53)	0.0026(6)	0.0057(16)	0.0100(18)	0.0005(7)	0.0035(8)	−0.0013(3)
C(54)	0.0034(6)	0.0080(19)	0.0030(10)	0.0012(9)	0.0006(6)	0.0003(10)
O(61)	0.0015(3)	0.0081(11)	0.0042(7)	0.0002(4)	0.0012(3)	0.0015(7)
N(61)	0.0013(3)	0.0064(12)	0.0031(7)	−0.0001(4)	0.0015(4)	−0.00030(7)
C(61)	0.0015(4)	0.0068(15)	0.0024(8)	0.0007(6)	0.0009(4)	−0.0009(8)
C(62)	0.0014(4)	0.0063(15)	0.0046(11)	0.0002(6)	0.0010(5)	0.0018(10)
C(63)	0.0020(5)	0.0105(22)	0.00502(12)	−0.0013(8)	0.0017(6)	−0.0002(13)
C(64)	0.0016(4)	0.0090(20)	0.0051(13)	−0.0005(7)	0.0004(6)	0.0004(12)
Cl(1)	0.0033(2)	0.0089(5)	0.0069(4)	−0.0013(2)	0.0034(2)	−0.0014(3)
Cl(2)	0.0029(2)	0.0100(6)	0.0100(5)	−0.0010(2)	0.0034(2)	−0.0014(4)
O1(1)	0.0063(8)	0.0162(23)	0.0173(21)	−0.0020(10)	0.0090(12)	−0.0038(17)
O1(2)	0.0080(10)	0.0172(25)	0.0139(20)	−0.0042(12)	0.0081(12)	−0.0062(17)
O1(3)	0.0088(12)	0.0190(29)	0.0193(27)	0.0041(14)	0.0096(15)	0.0065(22)
O1(4)	0.0039(7)	0.0513(6)	0.0096(18)	−0.0019(16)	−0.0003(9)	−0.0041(27)
O2(1)	0.0077(10)	0.0187(28)	0.0168(23)	−0.0026(12)	0.0092(13)	−0.0028(19)
O2(2)	0.0060(9)	0.0148(24)	0.0245(31)	−0.0013(10)	0.0086(14)	−0.0076(21)
O2(3)	0.0073(12)	0.0416(57)	0.0313(47)	−0.0116(22)	0.0096(20)	−0.0092(42)
O2(4)	0.0077(12)	0.0466(61)	0.0116(23)	0.0101(23)	−0.0008(13)	0.0046(30)

atoms are listed in Table 1. See also 'Supplementary material'.

Results

Synthesis of the compound

The complex is an H-T isomer as shown by the X-ray analysis. The complex is stable in acetonitrile, but is unstable towards water, and a 1:1 acetonitrile–water solution gradually precipitates brown powder due to decomposition of the compound. The decomposition seems to be accelerated by light. An attempt was made to observe the decomposition process by ^{195}Pt NMR spectroscopy, however, the decomposition products could not be isolated and therefore the peaks appearing during the decomposition could not be assigned. We attempted to synthesize an H-H isomer via several routes including that reported for H-H $[Pt_2(bpy)_2(1\text{-}MeU)_2]^{2+}$ [1], however none of them led to successful synthesis. The NMR and UV–Vis spectra show that the acetonitrile solution is stable at room temperature for at least a week.

Crystal structure

The structure of the complex cation with the atomic numbering scheme is shown in Fig. 1. The complex is an H-T dimer and each platinum atom is coordinated in a square planar way by two nitrogen atoms of bpy and a nitrogen, oxygen atom of the α-pyrrolidonate ligands. The H-T binuclear structure is analogous to those of previously reported H-T dimers, $[Pt(II)_2(NH_3)_4L_2]^{2+}$ (L is α-pyridonate [18], 1-methylthyminate [19] and 1-methyluracilate [20]). Crystal packing in the unit cell is shown in Fig. 2.

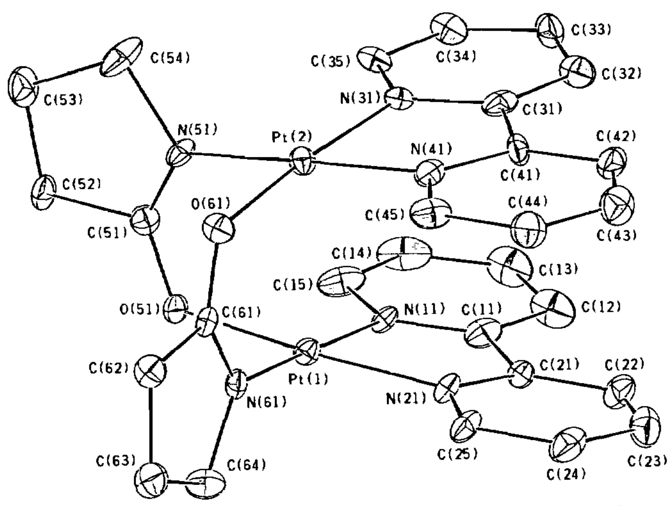

Fig. 1. Molecular structure of H-T $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2]^{2+}$. The thermal ellipsoids are drawn at 30% probability level.

UV–Vis spectrum and electrochemistry

The UV–Vis spectrum of $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$ in acetonitrile is shown in Fig. 3. The absorption band at around 300 nm is the π–π^* transition of bpy. The cyclic voltammogram (Fig. 4) of the complex shows a pair of irreversible waves at $E_{cp} = 0.84$, $E_{ap} = 1.17$ and $E_{1/2}$ ($= (E_{ap} + E_{cp})/2$) $= 1.01$ V versus SCE. Although we could not determine the electron number involved in the redox wave by coulometry since the bulk electrolytic oxidation at 1.4 V showed no definite end point, the redox wave seems to correspond to a two-electron reaction between Pt(II) and Pt(III) dimers as compared to the analogous Pt(II) amidate-bridged dimer complexes [3].

NMR studies

The ^1H–^{13}C COSY NMR spectrum is shown in Fig. 5 and the chemical shifts and the assignments are presented in Table 2. The ^{195}Pt chemical shift is presented in Table 3 together with those of other amidate-bridged Pt(II) binuclear complexes.

FAB mass spectrometry

The FAB mass spectrum of the present complex is shown in Fig. 6. Calculated *m/e* values for the expected fragments are listed in Table 4.

Discussion

Molecular and crystal structure

The complex cation is, as shown in Fig. 1, an H-T isomer. The Pt–Pt distance, the dihedral angle (τ) between the two platinum coordination planes and the average torsion angle (ω) about the Pt–Pt vector are

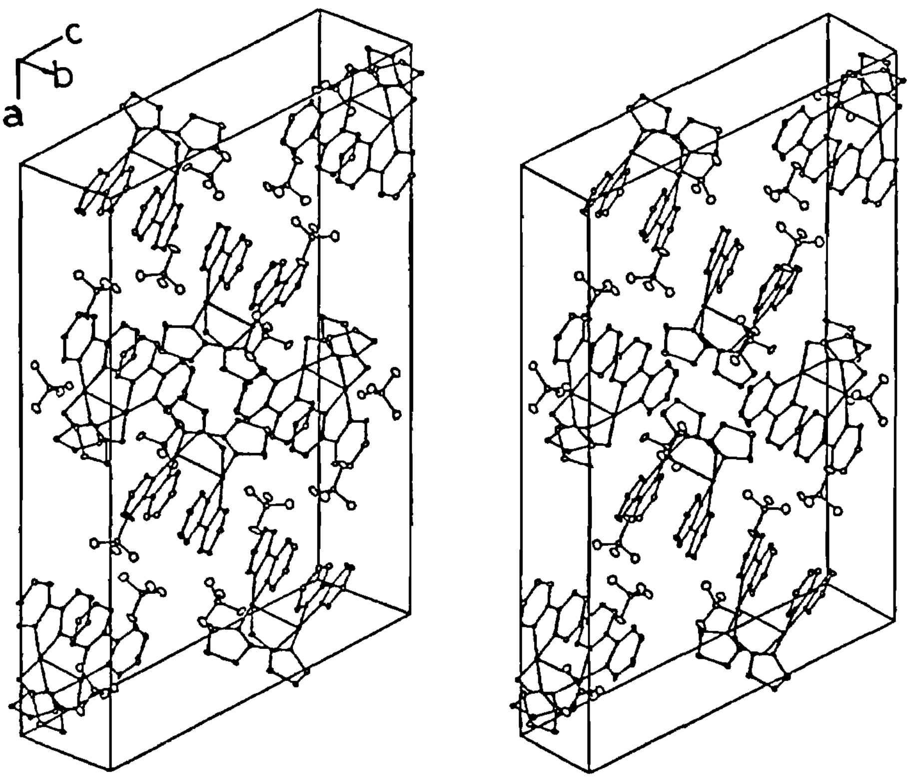

Fig. 2. Crystal structure of H-T $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$.

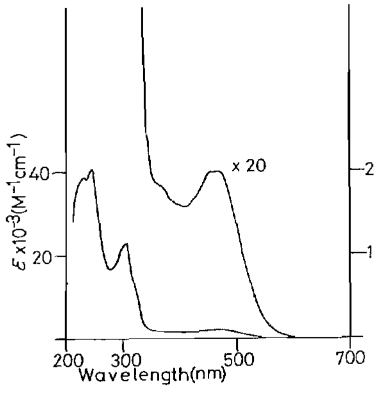

Fig. 3. UV–Vis spectrum of H-T $[Pt_2(bpy)_2(C_4H_6NO)_2](ClO_4)_2$ in acetonitrile (4 mM).

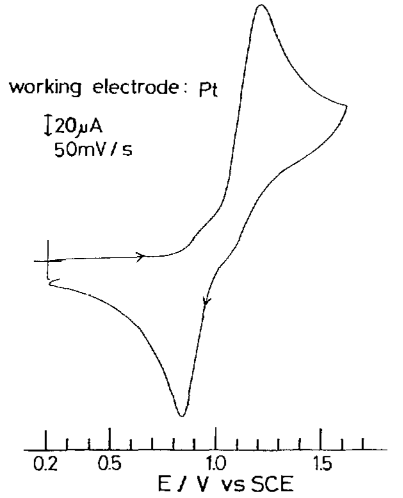

Fig. 4. Cyclic voltammogram of H-T $[Pt_2(bpy)_2(C_4H_6NO)_2](ClO_4)_2$ in acetonitrile (a 4 mM solution containing 0.1 M Bu_4NClO_4).

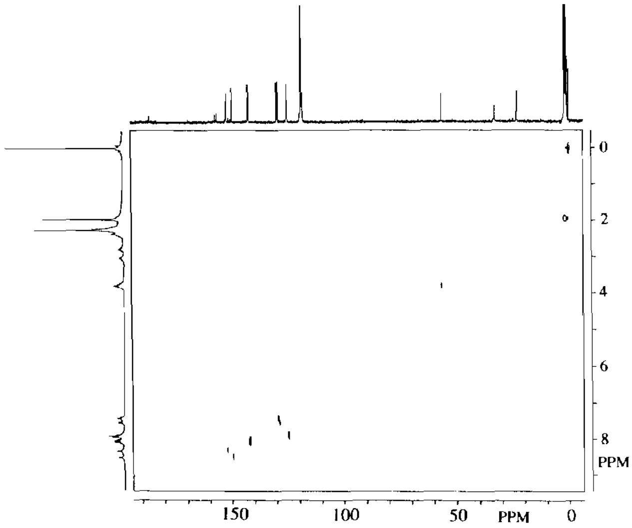

Fig. 5. ^1H–^{13}C COSY NMR spectrum in acetonitrile-d_3.

TABLE 2. ^{13}C chemical shifts and their assignments

Chemical shift (ppm)	Assignment
23.19	α-pyrrolidonate C(53) and C(63)
33.03	α-pyrrolidonate C(52) and C(62)
56.49	α-pyrrolidonate C(54) and C(64)
124.66 125.09	bpy C(12), C(22), C(32) and C(42)
128.61 129.46	bpy C(14), C(24), C(34) and C(44)
142.10 142.41	bpy C(13), C(23), C(33) and C(43)
149.57 152.17	bpy C(15), C(25), C(35) and C(45)
156.34 157.16	bpy C(11), C(21), C(31) and C(41)
186.27	α-pyrrolidonate C(51) and C(61)

TABLE 3. ^{195}Pt NMR chemical shifts in amidate-bridged Pt(II) binuclear complexes

Compound	^{195}Pt NMR δ (ppm)	Reference
$[Pt_2(bpy)_2(C_4H_6NO)_2](ClO_4)_2$ α-pyrrolidone, H-T dimer	−1710	this work
$[Pt_2(NH_3)_4(C_4H_6NO)_2]_2(PF_6)_3 \cdot H_2O$ α-pyrrolidone, H-T dimer	−1940	10
$[Pt_2(NH_3)_4(C_4H_6NO)_2]_2(PF_6)_3 \cdot H_2O$ α-pyrrolidone, H-H dimer	−1396 −2446	10
$[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](NO_3)_2 \cdot 1.5H_2O$ 3,3-dimethylglutarimide, H-T dimer	−1770.38	21
$[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2 \cdot 2H_2O$ α-pyridone, H-T dimer	−1810	18
$[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2 \cdot 2H_2O$ α-pyridone, H-H dimer	−1308 −2261	18

tabulated in Table 5. Selected interatomic distances are listed in Table 6. The coordination geometries of both Pt atoms are square planar with rather small deviations of the ligating atoms from the best coordination planes determined by the five atoms. The coordination angles around the Pt atoms somewhat deviate from 90°, since the bite angles for bpy are 79.7° (coordinated to Pt(1)) and 79.5° (coordinated to Pt(2)), and accordingly the other three angles for each Pt atom are close to or larger than 90°. Comparison of the two Pt–N(bpy) distances for both Pt atoms reveals that the distance *trans* to the amidate-nitrogen atom is always longer (0.01 ~ 0.02 Å) than those *trans* to the amidate-oxygen atom. This is a reflection of the larger *trans* influence of an amidate-nitrogen atom than that of an amidate-oxygen atom.

The two Pt coordination planes are tilted by 21.2° (τ value in Table 5) and the two coordination planes

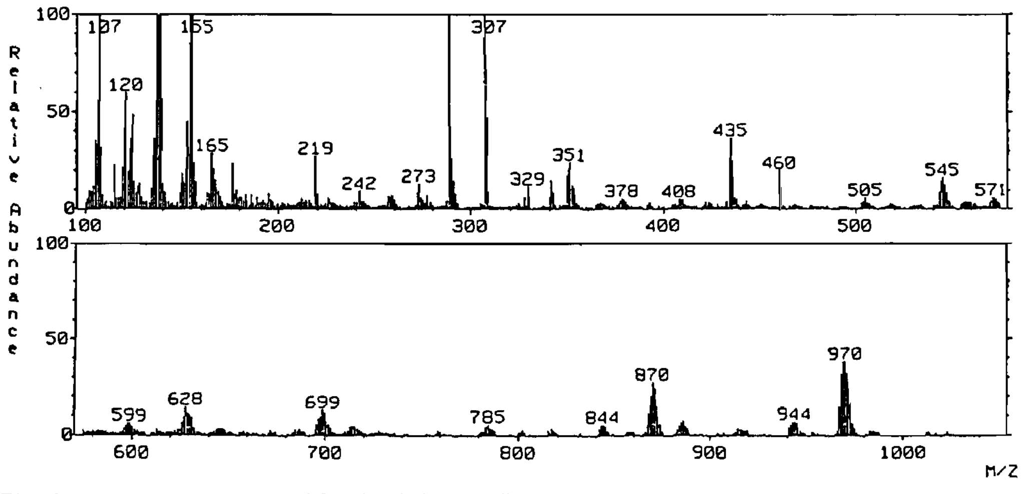

Fig. 6. FAB mass spectrum of $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)_2$.

TABLE 4. Calculated *m/e* values for expected fragments

Fragments	*m/e*
$[Pt_2(bpy)_2(C_4H_6NO)_2]^{2+}$	435
$[Pt_2(bpy)_2(C_4H_6NO)]^+$	786
$[Pt_2(bpy)_2(C_4H_6NO)_2]^+$	870
$\{[Pt_2(bpy)_2(C_4H_6NO)](ClO_4)\}^+$	885
$\{[Pt_2(bpy)_2(C_4H_6NO)_2](ClO_4)\}^+$	969
$\{[Pt_2(bpy)_2(C_4H_6NO)_2]I\}^+$	997

are canted against each other to open at the bpy sites. The Pt–Pt separation is 2.899(2) Å. The tilt angle, the average torsion angle about the Pt–Pt vector and the Pt–Pt distance are appreciably small compared to the previously reported values, as shown in Table 5. The stacking effect of the two bpys seems to be responsible for these small structural values. The present structure has therefore a remarkably small torsional strain, compared to the previously reported H-T and H-H Pt(II) dimer structures. The two bpys are almost overlapped and the torsion angles for N(21)–Pt(1)–N(41) and N(11)–Pt(2)–N(31) are less than 10°.

The structure of the H-T complex is essentially optically active and a unit cell contains a racemic mixture of four molecules of each isomer. In the crystal lattice (Fig. 2) two H-T dimers are located as if to form a tetramer with their bpy ligands stacked on each other.

TABLE 5. Comparison of the geometric properties of amidate-bridged binuclear Pt(II) complexes

Compound	Pt–Pt distance (Å)	Dihedral angle[a] (°)		Reference
		τ	ω	
$[Pt_2((C_5H_4N)_2)_2(C_4H_6NO)_2](ClO_4)_2$ α-pyrrolidone, H-T dimer	2.899(2)	21.1	−5, −10	this work
$[Pt_2(NH_3)_4(C_4H_6NO)_2]_2(PF_6)_3(NO_3)\cdot H_2O$ α-pyrrolidone, H-H dimer	3.033(2)	35.9	17.9	10
$[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2\cdot 2H_2O$ α-pyridone, H-T dimer	2.8981(5)	28.8	13.0	8
$[Pt_2(NH_3)_4(C_5H_4NO)_2](NO_3)_2\cdot 2H_2O$ α-pyridone, H-H dimer	2.8767(7)	30.0	20.3	8
$[Pt_2(NH_3)_4(C_7H_{10}NO_2)_2](NO_3)_2\cdot 1.5H_2O$ 3,3-dimethylglutarimide, H-T dimer	2.930(2)	36.0	21.2	21
$[Pt_2(NH_3)_4(C_6H_7N_2O_2)_2](NO_3)_2\cdot H_2O$ 1-methylthymine, H-T dimer	2.974(1)	36.1	13.8	19
$[Pt_2(NH_3)_4(C_5H_5N_2O_2)_2](NO_3)_2\cdot 3H_2O$ 1-methyluracil, H-T dimer	2.954(2)	35.8	19.1	20
$[Pt_2(NH_3)_4(C_5H_6N_3O)_2](NO_3)_2\cdot 2H_2O$ 1-methylcytosine, H-T dimer	2.981(2)	34	16	22
$[(NH_3)_2Pt(C_5H_5N_2O_2)_2Pt(bpy)](NO_3)_2\cdot 3H_2O$ 1-methyluracil, H-H dimer	2.929(1)	30.4	10.2	23

[a] τ is the dihedral angle between the two adjacent coordination planes and ω is the torsion angle about the Pt–Pt vector.

TABLE 6. Selected interatomic distances (Å)

Pt(1)–Pt(2)	2.899(2)	Pt(1)···Pt(1)′	3.765(2)
Pt(1)–N(11)	2.00(3)	Pt(2)–N(31)	2.00(2)
Pt(1)–N(21)	1.98(3)	Pt(2)–N(41)	2.01(3)
Pt(1)–N(61)	2.03(3)	Pt(2)–N(51)	2.01(2)
Pt(1)–O(51)	2.02(2)	Pt(2)–O(61)	2.01(2)
N(11)–N(31)	3.46(2)	C(11)–C(31)	3.75(4)
C(12)–C(32)	3.88(5)	C(13)–C(33)	3.86(4)
C(14)–C(34)	3.61(5)	C(15)–C(35)	3.51(4)
Ligand geometry			
N(11)–C(11)	1.31(3)	N(21)–C(21)	1.34(3)
N(11)–C(15)	1.42(3)	N(21)–C(25)	1.41(3)
C(11)–C(12)	1.42(4)	C(21)–C(22)	1.36(4)
C(12)–C(13)	1.41(4)	C(22)–C(23)	1.40(4)
C(13)–C(14)	1.41(5)	C(23)–C(24)	1.40(4)
C(14)–C(15)	1.41(4)	C(24)–C(25)	1.41(4)
C(11)–C(21)	1.50(3)		
N(31)–C(31)	1.38(3)	N(41)–C(41)	1.37(3)
N(31)–C(35)	1.36(2)	N(41)–C(45)	1.38(3)
C(31)–C(32)	1.39(4)	C(41)–C(42)	1.37(4)
C(32)–C(33)	1.44(3)	C(42)–C(43)	1.40(3)
C(33)–C(34)	1.36(4)	C(43)–C(44)	1.40(5)
C(34)–C(35)	1.36(4)	C(44)–C(45)	1.42(4)
C(31)–C(41)	1.49(3)		
O(51)–C(51)	1.29(2)	O(61)–C(61)	1.27(2)
N(51)–C(51)	1.26(2)	N(61)–C(61)	1.30(2)
N(51)–C(54)	1.52(3)	N(61)–C(64)	1.44(3)
C(51)–C(52)	1.58(3)	C(61)–C(62)	1.54(3)
C(52)–C(53)	1.56(3)	C(62)–C(63)	1.53(3)
C(53)–C(54)	1.64(4)	C(63)–C(64)	1.54(4)
Anion geometry			
Cl(1)–O1(1)	1.27(3)	Cl(2)–O2(1)	1.34(3)
Cl(1)–O1(2)	1.31(3)	Cl(2)–O2(2)	1.32(4)
Cl(1)–O1(3)	1.34(5)	Cl(2)–O2(3)	1.32(6)
Cl(1)–O1(4)	1.29(4)	Cl(2)–O2(4)	1.32(4)

However, the central Pt–Pt distance is 3.765(2) Å which is too long to be a bonding and therefore each dimeric complex is independent and there is no definite interaction between them.

Electrochemistry

The redox potential of $E_{1/2}=1.01$ V versus SCE for the present complex is significantly higher than that of the corresponding ammine (NH_3) complex, H-H and H-T $[Pt_2(NH_3)_4(\alpha\text{-pyrrolidonato})_2]^{2+}$ [10] (0.53 V versus SCE) and indicates that coordination of bpy considerably raises the redox potential as expected. The electrochemically oxidized product of the present compound is unstable and the solution precipitates decomposition products.

NMR studies

The ^{195}Pt NMR spectrum of the complex in acetonitrile clearly shows a single peak at −1710 ppm, which signifies that no isomerization from H-T to H-H occurs for the present complex, unlike the previously reported isomerization of H-H $[Pt_2(NH_3)_4L_2]^{2+}$ (L = α-pyrrolidonate [10], α-pyridonate [12]) to an H-T isomer in water, DMF and DMSO. Remeasurements of the solution of the present complex after a week showed no spectral change. From the comparison of the ^{195}Pt chemical shifts in Table 3, it is obvious that the present value is significantly higher than those of other amidate-bridged Pt(II) compounds, and indicates that the platinum atom is in an electron-poorer state, compared to other Pt(II) dimeric complexes. This fact corresponds to the result of the electrochemistry that the redox potential of the present complex is significantly higher, since the electron is backdonated from the Pt atom to the π^* orbital of bpy.

The ^{1}H–^{13}C COSY spectrum (Fig. 5) enables the ^{1}H assignments. All ^{1}H–^{13}C signals in the bpy ligands consist of two closely neighboring lines, which indicates the inequivalency of the two pyridine rings of a bpy ligand. The molecular structure in Fig. 1 shows that one pyridine ring is *trans* to the amidate-nitrogen atom, whereas the other ring is *trans* to the amidate-oxygen atom.

FAB mass spectroscopy

FAB mass spectroscopy is expected to provide a useful tool for the determination of molecular weights of multinuclear complexes. For those ionic complexes like the present compound, the fragmentation pattern is of particular interest and experience and accumulation of the data for such complexes would make the method a more powerful tool for the determination of molecular weights. Figures 6 and 7 show that, under the present conditions, the peak with the largest *m/e* value corresponds to $\{[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2](ClO_4)\}^+$ rather than $[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2]^{2+}$. On addition of KI or NaCl to the sample, the major peak shifts to $\{[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2]I\}^+$ (*m/e* = 997) and $\{[Pt_2(bpy)_2(\alpha\text{-pyrrolidonato})_2]Cl\}^+$ (*m/e* = 905), respectively, and this fact confirms the assignment of the original peak as a perchlorate-paired monocationic fragment. An isotopic distribution pattern was calculated (Fig. 7) for the peaks with *m/e* = 970 and 870, which also justifies the assignment of the peaks. From these data, FAB mass spectroscopy seems useful for this class of cationic binuclear complexes. For amidate-bridged tetranuclear complexes like platinum blues [2, 12] and octanuclear platinum blue complexes [24], we are still searching for the best conditions to obtain the correct molecular weight.

Conclusions

Amidate-bridged Pt(II) binuclear complexes have usually been reported to isomerize in solution between

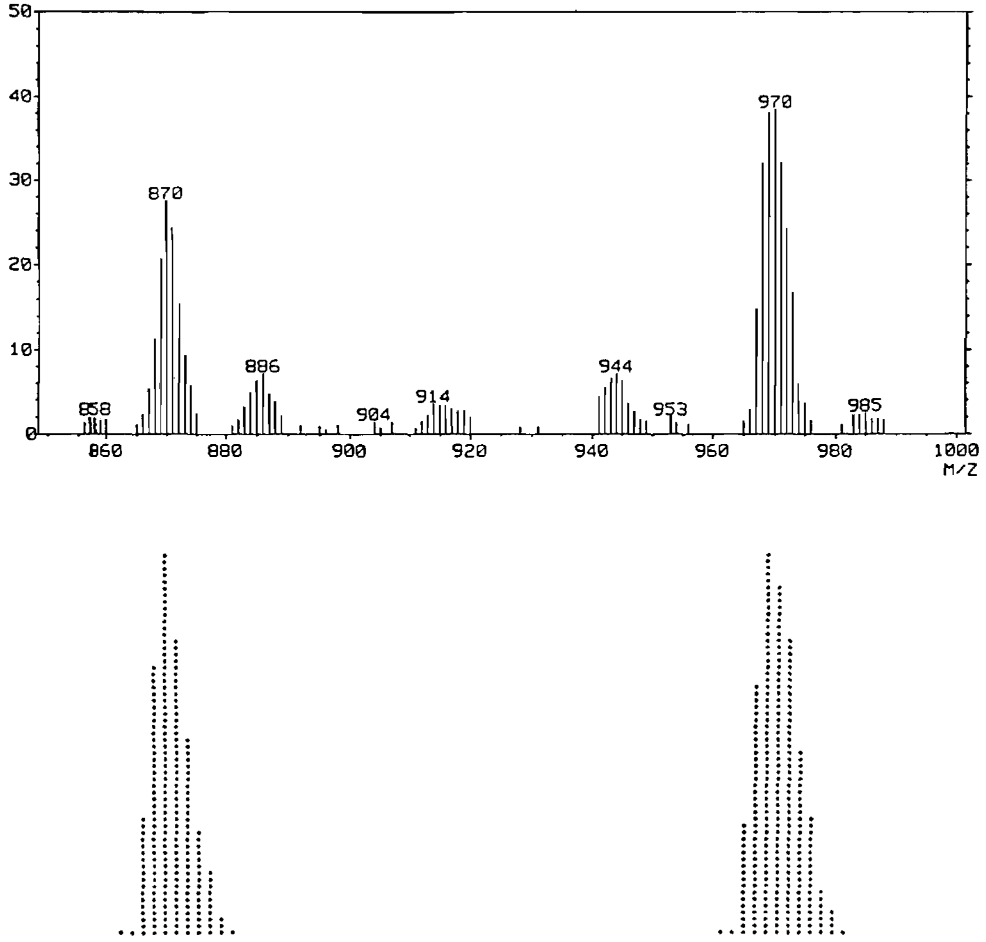

Fig. 7. The observed (above) and calculated (below) mass distribution patterns.

H-H and H-T isomers in H_2O, DMF or DMSO [10, 12]. The present complex is the first H-T complex that does not isomerize at least in acetonitrile. Although it would be interesting to know whether the isomerization takes place in an aqueous solution, it was impossible to test the possibility, since the present complex does not dissolve in H_2O, and is gradually decomposed in a 1:1 acetonitrile–water solution. We do not know at present why the complex is so unstable against water. It should be noted that the very unstrained amidate-bridged geometry and the lack of isomerization of the present complex strongly support the isomerization mechanism and the relationship between the isomerization rate and the steric strain of the amidate ligand which have been recently reported by O'Halloran and Lippard [12]. They conclude from their ^{195}Pt NMR studies that the isomerization takes place via an intramolecular mechanism and the rate-determining step is the cleavage of the Pt–N(amidate) bonding. They state that typically inert and thermodynamically stable Pt–N bonding can be labile in this class of complexes and the lability depends possibly on the steric strain forced by the bridging geometry of the amidate ligand [12]. The present complex with remarkably little strain and no isomerization clearly supports their conclusions.

Supplementary material

Positional and thermal parameters for the hydrogen atoms and the observed and calculated structure factors are available from the authors on request.

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