Synthesis and Structural Characterization of Trinuclear, Amidate-Bridged Heterobimetallic Complexes $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2M]X_n$ (M = Mn, Fe, Co, Ni, Cu; X = BF_4^-, ClO_4^-; n = 2 or 3)

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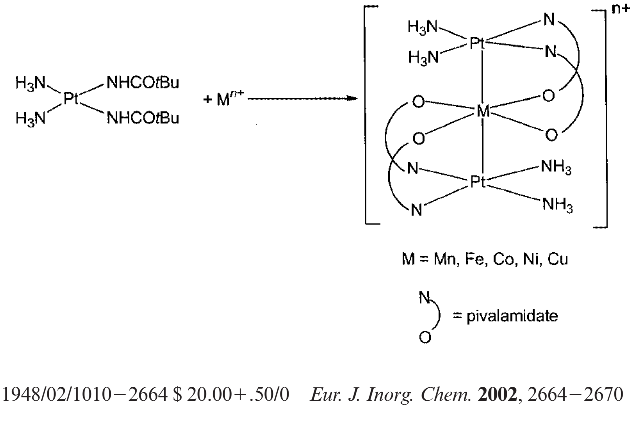
Keywords: N ligands / Bridging ligands / Platinum / Manganese / Iron / Cobalt / Nickel / Copper

A family of trinuclear heterometallic complexes of the formula $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2M]X_n$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}; X = BF_4^-, ClO_4^-) have been prepared by reacting $[Pt(NH_3)_2(NHCOtBu)_2]\cdot 2H_2O$ and the corresponding metal ions in water. They were characterised by elemental analysis, and their structures were determined by X-ray crystallography. The crystal structures of all the complexes consist of trinuclear $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2M]^{n+}$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) cations with M located at the centre. The platinum atoms are linked to the central metal atom through their amidate ligands also by Pt–M interactions. The coordination sphere of the Pt atom is completed by two NH_3 and two amidate ligands in *cis* positions to each other. The central heterometal ions are coordinated by four oxygen atoms of the amidate ligands, adopting either a square-planar or a tetrahedral conformation. Crystal structure determinations of all the complexes revealed extensive systems of N–H···O hydrogen bonds between the coordinated NH_3 ligands and the counteranions.

Introduction

Heterometallic cluster complexes containing direct M−M interactions are expected to create a new era of transition metal chemistry, especially in the fields of multimetallic catalysis and functional materials, due to their versatile chemical and physical properties, and thus the chemistry of heterotransition metal complexes has received great attention in recent years.[1] Multimetallic complexes are also promising precursors in developing nanostructured materials, including molecular-scale electronic, optical, and chemical devices.[2] A number of these complexes have been shown to exhibit unique spectroscopic properties that are associated with the metal-metal interactions.[3]

We became interested in $[Pt(NH_3)_2(NHCOtBu)_2]\cdot 2H_2O$[4] because this compound is the core of a number of amidate-bridged dimeric and oligomeric platinum complexes containing metal-metal interactions and mixed oxidation states of the metals.[5] Partially oxidized tetranuclear platinum complexes have been applied to the activation of C−H bonds of ketones to give ketonylplatinum(III) dinuclear complexes, and the coordination of olefins in water to give hydroxyalkylplatinum complexes.[6] It was also found that amidate-bridged Pt^{III} complexes catalyze the oxidation of terminal olefins to ketones in acidic water and promote the dihydroxylation of alkenes in neutral aqueous solutions.[7] We have recently described the preparation and structural characterization of $[Pt(NH_3)_2(NHCOtBu)_2]\cdot 2H_2O$, which acts as a versatile building block for the construction of dinuclear platinum and platinum-palladium complexes.[4] In addition, many transition metal ions of the first row are known to play an important role in oxidation reactions. Therefore, it was of interest to prepare amidate-bridged heterometallic compounds with the transition metal ions of the first row, and to study their redox chemistry and catalysis. As a continuation of our work on the platinum amidate chemistry, we report here the preparation and X-ray structural characterization of heterometallic trinuclear complexes of the formula $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2M]X_n$ (M = Mn^{2+} **1**, Fe^{3+} **2**, Co^{2+} **3**, Ni^{2+} **4**, Cu^{2+} **5** and **6**; X = BF_4^-, ClO_4^-).



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Results and Discussion

Synthesis

The square-planar platinum complex $[\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2]\cdot 2H_2O}$, readily prepared by basic hydrolysis of $[\mathrm{Pt(NH_3)_2(NC}t\mathrm{Bu)_2](ClO_4)_2}$, reacts with Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+} or Cu^{2+} salts in water to form trinuclear complexes with the formula $[\{\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2}\}_2\mathrm{M}]X_n$, where X is either perchlorate or tetrafluoroborate. Remarkably, regardless of the Pt:M ratio (1:1 or 2:1) the trinuclear Pt_2M complexes were formed exclusively in high yield. Attempts to prepare the platinum-copper dimeric complex with the formula $[\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2Cu(en)](ClO_4)_2}$ by reacting $[\mathrm{Cu(en)_2(H_2O)](SO_4)}$ with $[\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2]\cdot 2H_2O}$ in a 1:1 ratio were not successful, and $[\{\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2}\}_2\mathrm{Cu}](\mathrm{ClO_4})_2$ was the only isolated complex. However, both dimeric *cis*-$[\mathrm{(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]SO_4\cdot 4.5H_2O}$,[8] and trimeric *cis*-$[\mathrm{(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2}]^{2+}$ (1-MeU = 1-methyluracilato)[9] have long been known. Reaction of $\mathrm{FeSO_4\cdot 7H_2O}$ with $[\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2]\cdot 2H_2O}$ did afford the red $\mathrm{Pt_2^{II}Fe^{III}}$ complex rather than $\mathrm{Pt_2^{II}Fe^{II}}$, and a gradual colour change in water was observed from light green to red.

Structural Characterisation

Since the NMR spectroscopic data of the paramagnetic complexes were not particularly informative, suitable single crystals were grown by slow evaporation and cooling of an H_2O/acetone solution. All of the complexes were characterised by X-ray diffraction analysis.

The crystal structures of all of the complexes consist of trinuclear $[\{\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2}\}_2\mathrm{M}]^{n+}$ (M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}) cations with M located at the centre. Within the cations each platinum atom is linked to the central heterometal atom through two amidate ligands and a Pt−M interaction. The coordination sphere of the Pt atom is completed by two NH_3 and two amidate ligands in *cis* positions to each other. The central metal atoms are coordinated by four oxygen atoms of the amidate ligands. Two pairs of pivalamidate ligands are arranged head-to-head. The head-to-head orientation of the amidate ligands in these complexes is not straightforward from X-ray crystallographic arguments, but is reasonable on the basis of the method of preparation and the properties of the central metal ions. The Pt−N bond lengths and N−Pt−N angles are normal and similar to the values found in the starting compound $[\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2]\cdot 2H_2O}$. These data as well as the M−O distances and O−M−O angles are listed in Table 1 and 2. The Pt−M−Pt axes in **1b, 4−7** are roughly perpendicular to both of the coordination planes of Pt and M. In complex **1b**, **4−7**, the Pt−M−Pt axes are virtually linear with a Pt−M−Pt angle of 180°, whereas in **1a** and **3**, the Pt−M−Pt axes are bent with a Pt−M−Pt angle of 114.13(7)° and 176.39(8)° for **1a** and **3**, respectively. The structures of the complexes with the linearly ordered Pt−M−Pt cores are essentially the same.

Crystal Structures of $[\{\mathrm{Pt(NH_3)_2(NHCO}t\mathrm{Bu)_2}\}_2\mathrm{Mn}](\mathrm{ClO_4})_2\cdot 4\mathrm{H_2O}$ (1)

Crystallographic analysis of the manganese complex revealed that the asymmetric unit comprises of one molecule of **1a** and half of a molecule of **1b**. The structure of **1b** is generated by the inversion centre (1/2, 0, 1/2) at Mn(2). The structure of the cations of **1a** and **1b** are illustrated in Figure 1a and 1b. It is interesting to note that in **1a** the central Mn atom adopts a tetrahedral geometry, which is completed by the four amidate oxygen atoms, or a bicapped tetrahedron when the two rather long Pt−Mn contacts are considered. In **1b**, however, the Mn ion adopts a square-planar geometry, or it may be viewed as octahedrally coordinated with the platinum atoms sitting above and below the coordination plane. The distance between the Pt and Mn

Table 1. Selected bond lengths (Å) for complexes **1−6**

Compound	$Pt-N_{amine}$	$Pt-N_{amide}$	M−O	C−N	C−O	Pt−M
1a	2.006(16)	2.031(12)	2.044(8)	1.327(16)	1.246(14	2.8807(18)
	2.028(11)	1.996(10)	2.084(9)	1.293(15)	1.298(14)	2.9995(18)
	2.049(13)	1.995(12)	2.088(10)	1.312(18)	1.268(14)	
	2.042(11)	1.989(10)	2.089(9)	1.315(16)	1.310(13)	
1b	2.026(13)	2.019(11)	2.074(10)	1.275(16)	1.246(16)	2.6644(5)
	2.071(12)	2.007(10)	2.110(9)	1.293(15)	1.305(15)	
2	2.066(10)	1.999(9)	1.950(8)	1.294(15)	1.314(14)	2.5566(15)
	2.079(9)	2.018(11)	1.983(8)	1.266(17)	1.283(15	2.5718(15)
	2.058(9)	1.993(10)	2.003(8)	1.333(16)	1.293(15)	
	2.046(10)	2.010(9)	2.025(8)	1.301(16)	1.318(15)	
3	2.046(6)	1.991(6)	2.023(4)	1.258(10)	1.295(8)	2.6197(4)
	2.055(6)	1.991(6)	2.054(4)	1.318(8)	1.241(7)	
4	2.064(9)	2.036(9)	2.005(7)	1.321(13)	1.263(13)	2.5870(4)
	2.051(9)	2.000(9)	2.008(7)	1.286(12)	1.279(11)	
5	2.058(5)	1.995(5)	1.949(4)	1.314(7)	1.263(7)	2.6795(3)
	2.053(5)	1.985(5)	1.964(4)	1.315(7)	1.267(6)	
6	2.047(6)	2.017(5)	1.958(4)	1.283(8)	1.271(8)	2.6957(3)
	2.059(5)	2.011(5)	1.960(4)	1.308(7)	1.273(7)	

Table 2. Selected bond angles (°) for complexes **1−6**

Angles	**1a**	**1b**	**2**	**3**	**4**	**5**	**6**
N−Pt−N	86.0(6) 93.6(6) 95.0(4) 85.5(5) 89.4(5) 89.6(5) 89.2(5) 91.9(6)	92.7(5) 93.8(5) 86.7(5) 86.8(5)	90.5(5) 88.1(4) 86.4(4) 94.9(4) 90.3(4) 87.9(4) 92.6(4) 89.2(4)	91.8(2) 92.6(2) 87.4(2) 88.0(2)	91.5(4) 87.8(4) 88.5(4 92.2(4)	90.2(2) 88.4(2) 92.8(2) 88.4(2)	91.4(2) 87.1(2) 88.4(2) 93.0(2)
O−M−O	145.4(4) 89.6(4) 101.6(4) 99.2(4) 101.3(4) 106.1(4)	89.0(5) 91.0(5)	96.6(4) 89.6(3) 86.8(4) 87.3(4)	89.7(2) 90.3(2)	89.0(3) 91.0(3)	90.84(18) 89.16(18)	89.12(19) 90.88(19)
Pt−M−Pt	114.12(6)	180.000(10)	176.40(8)	180.0	180.0	180.0	180.0

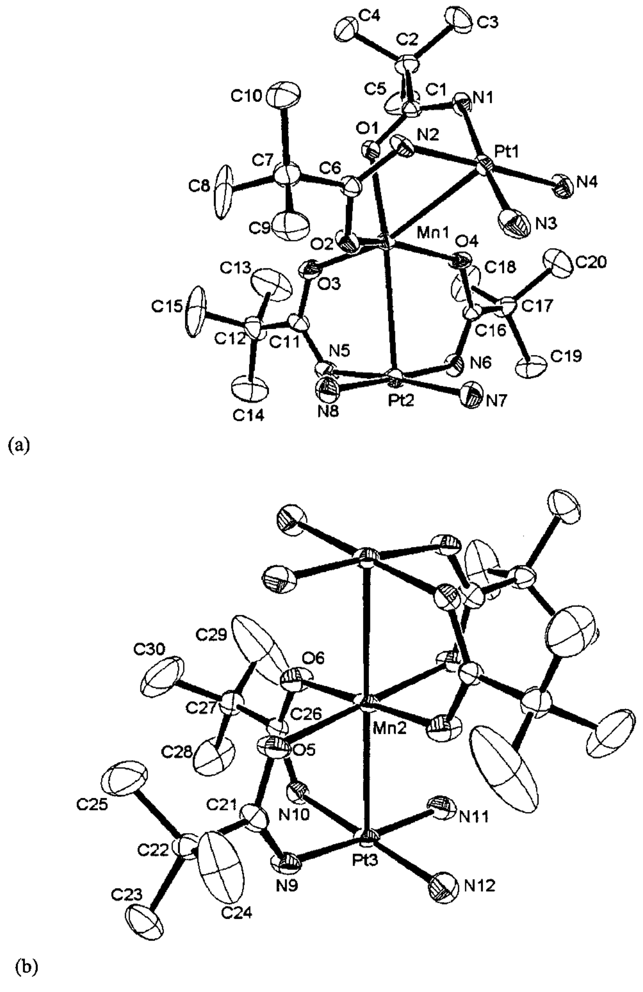

Figure 1. (a) ORTEP view of the bent [{Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$}$_2$Mn]$^{2+}$ cation in complex **1a**, showing the numbering of the atoms; (b) ORTEP view of the linear [{Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$}$_2$Mn]$^{2+}$ cation in complex **1b**, showing the numbering of the atoms; thermal ellipsoids are drawn at the 30% probability level

atoms within the cation of **1b** [2.6644(5)] is much shorter than those in the cation of **1a** [2.8807(18) Å and 2.9995(18) Å]. The Pt−Mn distance in **1b** is also shorter than that in [(NH$_3$)$_2$Pt(1-MeT)$_2$Mn(1-MeT)$_2$Pt(NH$_3$)$_2$]$^{2+}$ (1-Met = 1-methylthymine) [2.704(1) Å],[10] which has a similar Mn^{II} coordination environment, and it is even shorter than that in [(dppe)(CH$_3$)PtMn(CO$_5$)] (2.795 Å),[2a] in which the Pt−Mn bond is thought to be typical of a covalent single bond. The shorter Pt−Mn distance in **1b** is probably a consequence of the square-planar coordination of the Mn^{II} atoms which enables a closer approach to the square-planar Pt atoms than the Mn^{II} ion in the tetrahedral arrangement in **1a**. The Mn−O distances in both **1a** and **1b** fall in the range of 2.044(8)−2.110(9) Å, and are consistent with those found for octahedral complexes with oxygen atoms coordinated to Mn^{II} ions. The Pt−Mn−Pt axis in **1b**, which is linear by space group symmetry, is approximately perpendicular to both of the coordination planes of Pt and Mn. These coordination planes are tilted towards each other by an angle of 17.34°.

Crystals containing both **1a** and **1b** have four lattice water molecules in the unit cell. All of the water molecules and perchlorate ions participate in short contacts with the coordinated NH$_3$. The N−H···O contacts fall in the range of 3.011(15)−3.49(3) Å, suggesting hydrogen bonding. These hydrogen bonds link the cations, counteranions and the lattice water molecules into a two-dimensional network structure. Selected hydrogen bonds are listed in Table 3.

Crystal Structure of [{Pt(NH$_3$)$_2$(NHCO*t*Bu)$_2$}$_2$Fe](ClO$_4$)$_3$ (2)

The crystal structure of **2** is shown in Figure 2. The Pt$_2$Fe complex crystallises in a chiral orthorhombic space group $P2_12_12_1$. The platinum(II) and iron(III) atoms are held together through the four bridging pivalamidate ligands. The Pt−Fe−Pt is slightly bent with an angle of 176.40(8)°, but still close to a linear arrangement. The Pt−Fe distances are rather short [2.5566(15) Å and 2.5718(15) Å], and are similar to the values [2.5062(9)−2.673(4) Å] in the dppm-bridged Pt−Fe complexes.[11,12] The short Pt−Fe distances are attributed to the smaller Fe^{III} radius and the geometry requirement of the pivalamidate ligands. The coordination sphere of the Fe^{III} ion is completed by the four equatorial

Table 3. Selected hydrogen bonds (Å and °) for complexes **1−5**

D−H···A[a]	d(D−H)	d(H···A)	d(D···A)	<(DHA)
1				
N(3)−H(3D)···O(18)#2	0.89	2.29	3.13(3)	158.4
N(3)−H(3F)···O(22)#2	0.89	2.28	3.02(3)	140.6
N(4)−H(4E)···O(19)#3	0.89	2.25	3.111(18)	161.8
N(4)−H(4F)···O(4)	0.89	2.38	3.113(15)	139.9
N(7)−H(7A)···O(23)	0.89	2.28	3.14(3)	163.3
N(7)−H(7B)···O(22)#2	0.89	2.21	3.03(3)	153.0
N(7)−H(7C)···O(13)	0.89	2.26	3.04(2)	146.8
N(8)−H(8D)···O(2)	0.89	2.25	3.017(15)	144.1
N(8)−H(8E)···O(21)#4	0.89	2.22	3.10(3)	171.3
N(11)−H(11B)···O(17)#1	0.89	2.40	3.19(2)	147.7
N(11)−H(11C)···O(5)#1	0.89	2.21	3.011(15)	150.2
N(12)−H(12A)···O(6)#1	0.89	2.32	3.069(17)	142.4
N(12)−H(12B)···O(16)#1	0.89	2.27	3.04(2)	144.6
N(12)−H(12C)···O(11)	0.89	2.31	3.09(3)	146.3
2				
N(8)−H(8C)···O(2)	0.89	2.37	3.108(15)	141.0
N(8)−H(8B)···O(6)#5	0.89	2.19	3.074(16)	173.5
N(7)−H(7C)···O(7)#5	0.89	2.32	3.167(17)	157.8
N(7)−H(7B)···O(1)	0.89	2.17	2.906(12)	139.5
N(7)−H(7A)···O(9)#5	0.89	2.43	3.038(19)	126.3
N(4)−H(4B)···O(12)	0.89	2.37	3.046(15)	133.1
N(3)−H(3C)···O(3)	0.89	2.33	3.074(14)	141.0
N(3)−H(3B)···O(10)	0.89	2.40	3.031(17)	127.7
N(3)−H(3B)···O(12)	0.89	2.37	3.244(16)	166.6
3				
N(3)−H(3A)···O(1)#7	0.89	2.11	2.895(8)	146.9
N(3)−H(3B)···O(9)#8	0.89	2.30	3.157(10)	161.3
N(3)−H(3C)···O(5)#9	0.89	2.20	3.087(10)	175.3
N(4)−H(4A)···O(7)#8	0.89	2.31	3.158(15)	158.3
N(4)−H(4B)···O(9)#8	0.89	2.15	3.007(8)	160.7
N(4)−H(4C)···O(2)#7	0.89	2.16	2.937(7)	145.3
4				
N(3)−H(3D)···O(20)	0.89	2.25	3.120(15)	164.4
N(3)−H(3F)···O(1)	0.89	2.18	2.906(12)	139.0
N(4)−H(4D)···O(2)#10	0.89	2.13	2.899(12)	144.7
N(4)−H(4E)···O(15)#14	0.89	2.36	3.24(2)	169.0
N(4)−H(4F)···O(22)#15	0.89	2.29	3.16(2)	163.0
N(7)−H(7C)···O(3)#12	0.89	2.15	2.888(13)	140.3
N(8)−H(8D)···O(4)#12	0.89	2.20	2.923(12)	138.7
N(8)−H(8E)···O(11)	0.89	2.47	3.127(17)	131.4
N(11)−H(11A)···O(9)#16	0.89	2.29	3.178(15)	172.9
N(11)−H(11B)···O(14)#17	0.89	2.15	2.983(16)	154.5
N(11)−H(11C)···O(5)#11	0.89	2.09	2.865(12)	145.2
N(12)−H(12A)···O(6)	0.89	2.10	2.871(11)	145.0
N(12)−H(12C)···O(23)#12	0.89	2.43	3.32(2)	172.3
N(15)−H(15F)···O(7)#13	0.89	2.18	2.910(11)	139.0
N(16)−H(16A)···O(8)#13	0.89	2.13	2.906(10)	144.6
N(16)−H(16C)···O(20)#14	0.89	2.28	3.163(15)	169.6
5				
N(3)−H(3A)···O(1)#19	0.89	2.31	3.044(6)	139.3
N(3)−H(3B)···O(4)	0.89	2.31	3.181(10)	164.8
N(3)−H(3C)···O(5)#20	0.89	2.28	3.166(8)	172.5
N(4)−H(4A)···O(2)	0.89	2.22	2.983(6)	143.2
N(4)−H(4B)···O(6)#21	0.89	2.37	3.221(8)	161.1
N(4)−H(4C)···O(3)	0.89	2.39	3.143(9)	142.4

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + 1, -y, -z + 1$; #2: $x - 1, y, z - 1$; #3: $x - 1, y, z$; #4: $x, y, z - 1$; #5: $x + 1, y, z$; #6: $-x + 2, y + 1/2, -z + 3/2$; #7: $-x + 2, -y + 1, -z$; #8: $x + 1, y, z$; #9: $-x + 3/2, y + 1/2, -z + 1/2$; #10: $-x + 1, -y + 2, -z$; #11: $-x + 2, -y + 1, -z$; #12: $-x + 1, -y + 1, -z + 1$; #13: $-x + 2, -y + 2, -z + 1$; #14: $-x + 1, -y + 2, -z + 1$; #15: $x, y + 1, z - 1$; #16: $x + 1, y, z - 1$; #17: $x, y, z - 1$; #18: $x + 1, y + 1, z$; #19: $-x + 1, -y, -z + 1$; #20: $-x + 2, -y, -z + 1$; #21: $x - 1/2, -y + 1/2, -z + 1$.

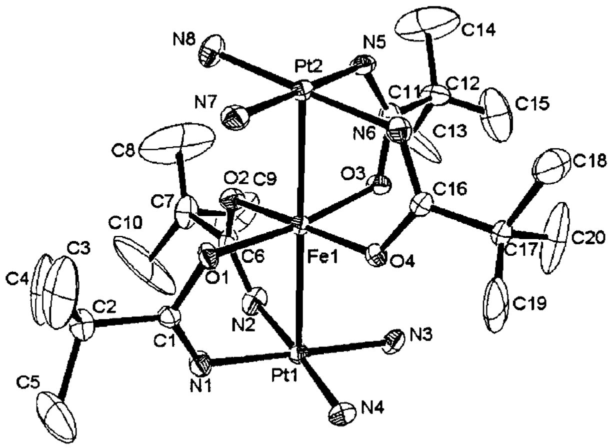

Figure 2. ORTEP view of the $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2Fe]^{3+}$ cation in complex **2**, showing the numbering of the atoms; thermal ellipsoids are drawn at the 30% probability level

oxygen atoms of the amidate ligands and the two platinum atoms sitting above and below the FeO_4 coordination plane, if the two Pt−Fe interactions are taken into account. The Pt−N and Fe−O bond lengths are normal and not very different from those observed in **1**. The whole molecules are also organized in the two-dimensional structure involving hydrogen bonds both of intercationic and between cations and perchlorate anions. Some hydrogen bonds are collected in Table 3.

Crystal Structure of $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2Co](ClO_4)_2$ (3)

Crystal data and selected bond lengths and angles are presented in Table 1 and 2. The structure of **3** consists of a centrosymmetric trinuclear Pt−Co−Pt core and two perchlorate counteranions (Figure 3). The Pt−Co bond length [2.6197(4) Å] within the cation is longer than those found in the Pt−Co clusters $[PtCo_2(CO)_7(cod)]$ [2.515(1) Å and 2.514(1) Å] and $[Pt_2Co_2(CO)_8(\mu_3\text{-}EtC_2Et)]$ [2.551(1) Å and 2.556(1) Å],[13] and is also longer than in the $(Ph_2P)_2NH$-

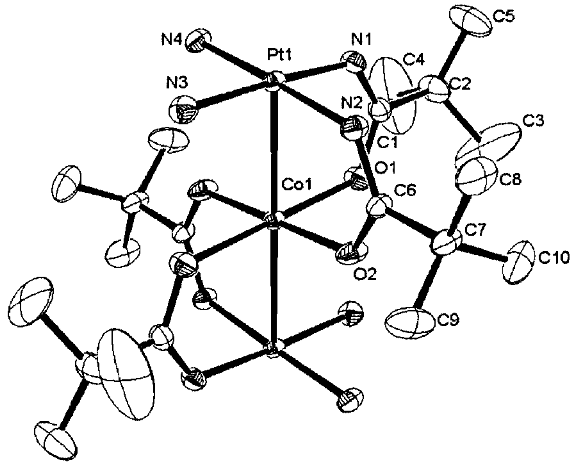

Figure 3. ORTEP view of the $[\{Pt(NH_3)_2(NHCOtBu)_2\}_2Co]^{2+}$ cation in complex **3**, showing the numbering of the atoms; thermal ellipsoids are drawn at the 30% probability level

bridged Pt−Co carbonyl complexes [2.531(2)−2.508(2) Å].[14] The cation and the counteranions are linked by hydrogen bonds between the coordinated NH_3 and the perchlorate oxygens. Intermolecular hydrogen bonds between the NH_3 and amidate oxygen atoms are also observed, and thus form two-dimensional networks.

Crystal Structure of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Ni](ClO_4)_2$ (4)

The asymmetric unit of the Pt_2Ni complex comprises four half units of a molecule of the complex, and their structures are generated by the inversion centre (1/2, 1, 0; 1/2, 1/2, 1/2; 1, 1/2, 0; 1, 1, 1/2) at Ni(1), Ni(2), Ni(3) and Ni(4), respectively. The four molecules are essentially the same, and one of the structures of the four cations is shown in Figure 4. The Pt−Ni−Pt angles in all of the four independent molecules are 180°. The platinum and nickel centres are bridged by triatomic NCO groups of the amidate ligands. Each nickel ion is coordinated to four oxygen and two platinum atoms at the axial sites. The *cis* O−N−O angles lie within the range 89.0(3)°−91.3(3)°. The *trans* O−Ni−O angles are both 180°. The Ni−O bond lengths [2.005(7) Å and 2.008(7) Å] are almost identical. The Pt−Ni distance within the cation is 2.5870(4) Å. The hydrogen atoms of the coordinated NH_3 ligands are engaged in hydrogen bonding interactions with the oxygen atoms of the perchlorate anions, resulting in the formation of a three-dimensional network.

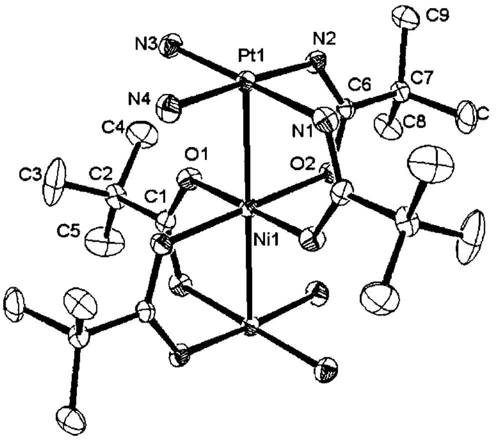

Figure 4. ORTEP view of the $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Ni]^{2+}$ cation in complex **4**, showing the numbering of the atoms; thermal ellipsoids are plotted at the 30% probability level

Crystal Structure of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Cu](ClO_4)_2$ (5) and $[\{Pt(NH_3)_2(NHCOBu)_2\}_2Cu](BF_4)_2$ (6)

Although the two complexes crystallise in different space groups, their structures are essentially the same. A molecular view of **5** is shown in Figure 5. Within the trimers, the Cu atoms are located at the special position (1/2, 0, 1/2) for both **5** and **6**. The Pt−Cu distances are 2.6795(3) Å and 2.6955(2) Å in **5** and **6,** respectively, and are therefore shorter than that in the Pt/Cu dimer, *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(H_2O)_2]^{2+}$,[9] and the Pt_2Cu trimer, *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Cu(1\text{-}MeU)_2Pt(NH_3)_2]^{2+}$ (1-MeU = 1-methyluracilato),[10] and much shorter than those in the platinum-copper complexes bridged by alkynyl ligands.[15]

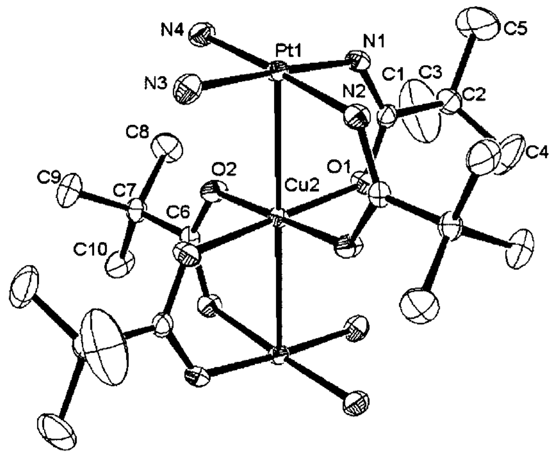

Figure 5. ORTEP view of the $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Cu]^{2+}$ cation in complex **5**, showing the numbering of the atoms; thermal ellipsoids are plotted at the 30% probability level

Similar to the complexes described above, the trinuclear cations and counteranions in **5** and **6** are connected by N−H···O and N−H···F hydrogen bonding, with N···O distances in the range from 2.983(6) Å to 3.221(8) Å, and the N−H···F distances from 2.961(9) to 3.092(13) Å. Short N−H···F and N−H···O contacts are presented in Table 3. The short contacts indicate strong hydrogen bonds between the hydrogen atoms of the NH_3 ligands and the fluorine or oxygen atoms of the anions. These interactions make two- and three-dimensional hydrogen bond networks for **5** and **6,** respectively.

All of the complexes presented here have provided unequivocal evidence for the formation of Pt−M (2:1) amidate-bridged complexes. X-ray diffraction analysis showed that the Pt atoms have an essentially planar conformation, and the central metal ions are similarly coordinated by four equatorial oxygen atoms with two platinum atoms occupying the two axial sites in **1b**, and **2**−**7**. The metal-metal distances in these complexes with linear Pt−M−Pt conformation are found to follow the order: Pt−Cu > Pt−Mn > Pt−Co > Pt−Ni > Pt−Fe. The metal-metal distances between the platinum and Mn^{II} (d^5), Fe^{III} (d^5), Co^{II} (d^7), Ni^{II} (d^8) and Cu^{II} (d^9) are rather short in complexes **2**−**7**. It was thought that these short intermetallic distances within the cations do not reflect a significant electronic interaction between the Pt and heterometals, and they are rather attributed to the geometric requirement caused by the two bridging ligands.[9] Most probably this also applies to our complexes. However, a weak metal-metal interaction should probably not be ruled out, on the basis of the Pt and the heterometal radii. The redox chemistry of these cationic trinuclear heterometallic complexes is currently being explored.

Experimental Section

General Remarks: $[Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\cdot 2H_2O]$ was prepared according to our published procedure.[4] All other chemicals and solvents were purchased and used as received.

Table 4. Crystal data and structure refinement for the complexes **1−6**

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{20}H_{56}Cl_2MnN_8O_{14}Pt_2$	$C_{20}H_{52}Cl_3FeN_8O_{16}Pt_2$	$C_{20}H_{52}Cl_2CoN_8O_{12}Pt_2$	$C_{20}H_{52}Cl_2N_8NiO_{12}Pt_2$	$C_{20}H_{52}Cl_2CuN_8O_2Pt_2$	$C_{20}H_{52}B_2CuF_8N_8O_4Pt_2$
Molecular weight	1148.70	1213.08	1116.71	1116.49	1121.32	1096.04
Crystal size	0.28 × 0.38 × 0.44	0.20 × 0.22 × 0.43	0.15 × 0.22 × 0.26	0.21 × 0.30 × 0.32	0.12 × 0.18 × 0.26	0.14 × 0.17 × 0.27
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$	*P*bca	$P2_1/n$
a, Å	11.4228(17)	10.8505(15)	13.451(2)	15.4742(10)	10.7665(17)	10.5401(7)
b, Å	34.480(5)	18.607(3)	11.0189(19)	15.5319(11)	18.178(3)	16.1012(11)
c, Å	16.128(3)	22.350(3)	16.056(3)	17.0866(12)	19.570(3)	12.1744(8)
α, deg	90	90	90	87.5750(10)	90	90
β, deg	91.481(3)	90	97.477(3)	83.976(2)	90	110.3520(10)
γ, deg	90	90	90	86.810(2)	90	90
V, $Å^3$	6350.1(17)	4512.5(11)	2359.6(7)	4074.9(5)	3830.3(11)	1937.1(2)
Z	6	4	2	4	4	2
$D_{calcd.}$ Mg/m^3	1.817	1.786	1.572	1.820	1.944	1.879
θ range	1.39−27.56	1.42−27.67	1.86−27.60	1.31−27.56	2.08−27.52	2.19−27.54
Reflections collected	38339	28144	14336	15008	16631	12043
Independent reflections (R_{int})	14358 (0.1407)	10323 (0.0728)	5355 (0.1025)	13829 (0.0355)	4386 (0.0904)	4416 (0.0313)
Goodness-of-fit	1.030	1.035	1.098	0.965	0.915	1.023
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0769, 0.1969	0.0501, 0.1485	0.0434, 0.1171	0.0463, 0.1201	0.0355, 0.0741	0.0327, 0.0937
$R1$, $wR2$ (all data)	0.1156, 0.2172	0.0600, 0.1553	0.0512, 0.1222	0.0732, 0.1318	0.0620, 0.0828	0.0454, 0.0988

Preparation of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Mn](ClO_4)_2\cdot4H_2O$ (1): A solution of $MnCl_2\cdot4H_2O$ (20 mg, 0.10 mmol) in 2 mL of water was added to a solution of $[Pt(NH_3)_2(NHCO\mathit{t}Bu)_2]\cdot2H_2O$ (93 mg, 0.20 mmol) in 1 mL of water. A pale-yellow precipitate was formed immediately by the addition of $NaClO_4$ (50 mg) to the pale-yellow solution. Yield: 95 mg (83%). $C_{20}H_{52}Cl_2N_8MnO_{12}Pt_2\cdot4H_2O$ (1148.70): calcd. C 20.28, H 5.10, N 9.46; found C 20.42, H 5.03, N 9.46.

Preparation of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Fe](ClO_4)_3$ (2): This compound was prepared from $FeSO_4\cdot7H_2O$ (27.8 mg, 0.10 mmol), $[Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\cdot2H_2O]$, and $NaClO_4$ (50 mg) as for **1**, and was isolated as red crystals. Yield: 98 mg (81%). $C_{20}H_{52}Cl_3FeN_8O_{16}Pt_2$ (1213.08): calcd. C 19.80, H 4.32, N 9.24; found C 19.90, H 4.15, N 9.26.

Preparation of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Co](ClO_4)_2$ (3): This compound was prepared from $Co(NO_3)_2\cdot6H_2O$, $[Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\cdot2H_2O]$ and $NaClO_4$ (50 mg) as for **1**, and was isolated as blue crystals. Yield: 102 mg (91%). $C_{20}H_{52}Cl_2CoN_8O_{12}Pt_2$ (1116.71): calcd. C 21.51, H 4.69, N 10.03; found C 21.36, H 4.55, N 9.78.

Preparation of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Ni](ClO_4)_2$ (4): This compound was prepared from $Ni(NO_3)_2\cdot6H_2O$ (18.2 mg, 0.1 mmol), $[Pt(NH_3)_2(NHCOBu)_2]\cdot2H_2O$ (46 mg, 0.1 mmol), and $NaClO_4$ (50 mg) as for **1**, and was isolated as light-green crystals. Yield: 80 mg, (72%). $C_{20}H_{52}Cl_2N_8NiO_{12}Pt_2$ (1116.49) C, 21.52, H 4.69, N 10.04; found C 21.75, H 4.88, N 9.70.

Preparation of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Cu](ClO_4)_2$ (5): This compound was prepared from $[Cu(en)(H_2O)](SO_4)$ (25 mg, 0.1 mmol), $[Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\cdot2H_2O]$ (46 mg, 0.1 mmol), and $NaClO_4$ (50 mg) as for **1**. The compound can also be prepared directly from $Cu(ClO_4)_2\cdot2H_2O$. Yield: 82 mg, (73%). $C_{20}H_{52}Cl_2CuN_8O_{12}Pt_2$ (1121.32): calcd. C 21.42, H 4.67, N 9.99; found C 21.46, H 4.43, N 9.82.

Preparation of $[\{Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\}_2Cu](BF_4)_2$ (6): This compound was prepared from $Cu(BF_4)_2\cdot6H_2O$ (23.7 mg, 0.10 mmol) and $[Pt(NH_3)_2(NHCO\mathit{t}Bu)_2\cdot2H_2O]$ (93 mg, 0.2 mmol) as for **1** and isolated as light green crystals. Yield: 84 mg (77%). $C_{20}H_{52}B_2CuF_8N_8O_4Pt_2$ (1096.04): calcd. C 21.92, H 4.78, N 10.22; found C 21.89, H 4.79, N 10.21.

X-ray Crystallographic Study: Data collection was performed on a Bruker Smart-CCD diffractometer by using monochromatized Mo-K_α radiation (λ = 0.71073 Å) at room temperature. Data reduction was performed by using the SAINT+ Version 6.02 software.[16] The data were corrected for absorption by using the program SADBAS within the SAINTPLUS package. The structures were solved by direct methods. This solution yielded metal atoms, N O, and some C atoms. Subsequent Fourier synthesis gave the remaining C-atom positions. The hydrogen atoms, except those of the amidate and water hydrogen atoms, were geometrically fixed, allowed to ride on their attached atoms, and refined with the XSHELL software.[17] The final refinement included anisotropic thermal parameters for all of the non-hydrogen atoms and converged to the *R*1 and *wR*2 values listed in Table 4.
CCDC-183354 (**1**), -183355 (**2**), -183356 (**3**), -183357 (**4**), -183358 (**5**) and CCDC-183359 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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[1] [1a] M. A. Bennett, M. Contel, D. C. R. Hockless, L. L. Welling, A. C. Willis, *Inorg. Chem.* **2002**, *41*, 844−855. [1b] T. Kawashima, K. Takai, H. Aso, T. Manabe, K. Takizawa, C. Kachi-Terajima, T. Ishii, H. Miyasaka, H. Matsuzaka, M. Yamashita, H. Okamoto, H. Kitagawa, M. Shiro, K. Toriumi, *Inorg. Chem.* **2001**, *40*, 6651−6655. [1c] L. Hao, J. Xiao, J. J. Vittal, R. J. Puddephatt, *Organometallics* **1997**, *16*, 2165−2174.

[2] [2a] V. W. W. Yam, K. L. Yu, K. M. C. Wong, K. K. Cheung, *Organometallics* **2001**, *20*, 721−726. [2b] S. Komiya, S. Muroi, M. Furuya, M. Hirano, *J. Am. Chem. Soc.* **2000**, *122*, 170−171.

[3] [3a] A. F. Heyduk, D. J. Krodel, E. E. Meyer, D. G. Nocera, *Inorg. Chem.* **2002**, *41*, 634−636. [3b] E. J. Fernández, P. G.

Jones, A. Laguna, J. M. López-de-Luzuriaga, M. Monge, J. Pérez, M. E. Olmos, *Inorg. Chem.* **2002**, *41*, 1056−1063. [3c] J. R. Berenguer, J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, *Organometallics* **2001**, *20*, 4847−4851. [3d] J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, *Inorg. Chem.* **2001**, *40*, 5415−5419.

[4] K. Matsumoto, K. Sakai, *Adv. Inorg. Chem.* **1999**, *49*, 375−427 and references therein.

[5] W. Chen, K. Matsumoto, *Inorg. Chim. Acta* in press.

[6] [6a] Y. Lin, H. Misawa, J. Yamada, K. Matsumoto, *J. Am. Chem. Soc.* **2001**, *123*, 569−575. [6b] K. Matsumoto, J. Matsunami, K. Mizuno, H. Uenura, *J. Am. Chem. Soc.* **1996**, *118*, 8959−8960.

[7] [7a] Y. Lin, S. Takeda, K. Matsumoto, *Organometallics* **1999**, *18*, 4897−4899. [7b] W. Chen, J. Yamada, K. Matsumoto, *Synth. Commun.* **2002**, *32*, 17−22. [7c] K. Matsumoto, Y. Nagai, J. Matsunami, K. Mizuno, T. Abe, R. Somazawa, J. Kinoshita, H. Shimura, *J. Am. Chem. Soc.* **1998**, *120*, 2900−2907.

[8] D. Neugebauer, B. Lippert, *J. Am. Chem. Soc.* **1982**, *104*, 6596−6601.

[9] B. Lippert, U. Thewalt, H. Schlhorn, D. M. L. Goodgame, R. W. Rollins, *Inorg. Chem.* **1984**, *23*, 2807−2813.

[10] B. Lippert, U. Schubert, *Inorg. Chim. Acta* **1981**, *56*, 15−20.

[11] [11a] X. L. R. Fontaine, G. B. Jacobsen, B. L. Shaw, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.* **1988**, 741−750. [11b] X. L. R. Fontaine, G. B. Jacobsen, B. L. Shaw, M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.* **1988**, 1185−1196.

[12] [12a] M. Knorr, P. B. Braunstein, A. DeCian, J. Fischer, *Organometallics* **1995**, *14*, 1302−1309. [12b] R. D. Adams, I. Arafa, G. Chen, J. C. Li, J. G. Wang, *Organometallics* **1990**, *9*, 2350−2357.

[13] R. D. Adams, G. Chen, W. G. Wu, J. G. Yin, *Inorg. Chem.* **1990**, *29*, 4208−4214.

[14] [14a] I. Bachert, I. Bartusseck, P. Braunstein, E. Guillon, J. Rose, G. Kickelbick, *J. Organomet. Chem.* **1999**, *588*, 144−151. [14b] I. Bachert, I. Bartusseck, P. Braunstein, E. Guillon, J. Rose, G. Kickelbick, *J. Organom. Chem.* **1999**, *580*, 257−264.

[15] [15a] V. W. W. Yam, K. L. Yu, K. K. Cheung, *J. Chem. Soc., Dalton Trans.* **1999**, 2913−2916. [15b] J. P. H. Charmant, J. Forniés, J. Gomez, E. Lalinde, R. I. Merino, M. T. Moreno, A. C. Orpen, *Organometallics* **1999**, *18*, 3353−3358. [15c] J. Forniés, E. Lalinde, A. Martin, M. T. Moreno, *J. Organomet. Chem.* **1995**, *490*, 179−188. [15d] P. Espinet, J. Forniés, F. Martinez, M. Tomas, E. Lalinde, M. T. Moreno, A. Ruiz, A. J. Welch, *J. Chem. Soc., Dalton Trans.* **1990**, 791−798.

[16] G. M. Sheldrick, *SHELXS-97, Program for X-ray Crystal Structure Solution*; University of Göttingen: Götingen, Germany, **1997**.

[17] G. M. Sheldrick, *SHELXL-97, Program for X-ray Crystal Structure Refinement*; University of Götingen: Götingen, Germany, **1997**.

Received February 21, 2002
[I02197]