Pt as Mediator of Strong Antiferromagnetic Coupling between Two Cu^{II} Ions in a Heteronuclear $Cu^{II}Pt^{II}Cu^{II}$ Complex of the Model Nucleobase 1-Methylcytosinate

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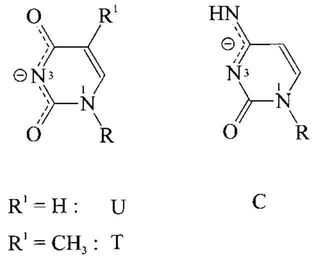
Abstract: The tetrakis(1-methylcytosine) complex $[Pt(1\text{-}MeC\text{-}N3)_4](NO_3)_2$ (**1**) in its head–tail–head–tail (*htht*) rotamer form binds upon deprotonation of the exocyclic amino group of 1-MeC, two Cu^{II} at either side of the central Pt^{II} to give trinuclear cations $[Pt(1\text{-}MeC^-)_4Cu_2X_2]^{n+}$ (**2**) with $X = Cl^-$, H_2O, NSC^-, N_3^-. X-ray crystal structure analyses of $[Pt(1\text{-}MeC^-)_4Cu_2(Cl)_{1.6}(H_2O)_{0.4}](NO_3)_{0.4}\cdot 1.6\,H_2O$ (**2a**) and $[Pt(1\text{-}MeC^-)_4Cu_2(H_2O)_2](NO_3)_2\cdot 3\,H_2O$ (**2b**) reveal short Cu–Pt distances of 2.519(2)–2.531(2) Å. These compounds are diamagnetic as a result of the strong exchange interaction ($J = 980 \pm 30\ cm^{-1}$ (**2a**)), despite a separation of approximately 5 Å between the Cu^{II} centers. MO considerations are in agreement with the assumption that Pt^{II} acts as a mediator between the two Cu^{II} centers. A second trinuclear complex derived from the *hhhh* rotamer of **1** containing both Co^{III} and Na^+ $[Pt(1\text{-}MeC^-)_4Co(H_2O)Na](NO_3)_2\cdot 2\,H_2O$ (**3**) has been isolated in very low yield and characterized by X-ray structure analysis. The Co^{III} center is bound to four amide N atoms and forms a bond to Pt (2.402(2) Å), whereas the Na^+ ion is bound to the four oxygen atoms of the nucleobase. A general route for the preparation of heteronuclear MPtM and MPtM′ compounds is described.

Keywords: copper · magnetic properties · metal–metal interactions · nucleobases · platinum

Introduction

Metal complexes with tridentate ligands and a linear trimetal core represent an extension of dinuclear complexes and are of current interest in particular with regard to the investigations on metal–metal interactions, the question of "bond stretch isomerism", and the preparation of "molecular wires".[1] The anionic N1-blocked pyrimidine nucleobases L = uracil (U), thymine (T), and cytosine (C) represent ligands with O,N,O and N,N,O donor sites that are, in principle, suitable for the stabilization of a linear trimetallic chain, analogous to the frequently used anions of bis(2-pyridyl)amine or bis(2-pyridyl)formamidine, which have N,N,N and N,N,N,N donor sets.



We have previously reported on tri- and polynuclear complexes containing these nucleobase ligands. In most cases trinuclear species of Pt_2M stoichiometry were formed through chelation of a heterometal ion by two *cis*-a_2PtL_2 entities (a = am(m)ine or a_2 = diamine) with only two of the donor sites of L being used (Scheme 1, a)).[2] In principle, a *trans*-a_2PtL_2

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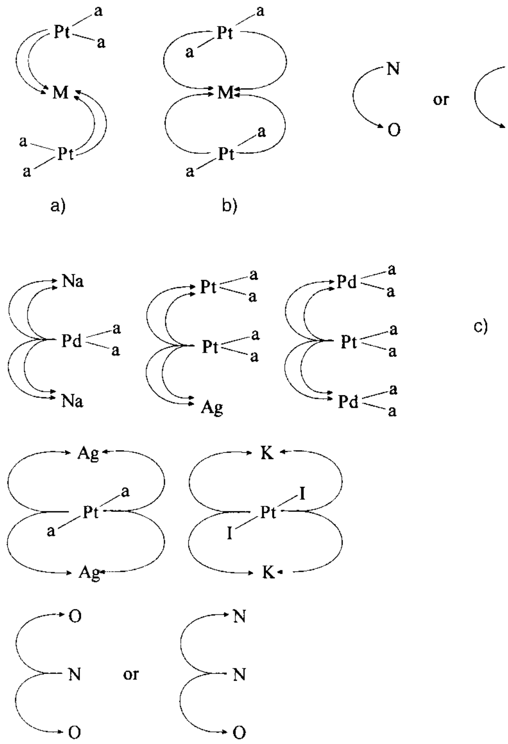
geometry (Scheme 1, b)) is also feasible, but thus far this geometry has only been observed in a (Pt_2Cu)-system with the nucleobases replaced by 2-pyridonate.[3] In a limited number of cases the stoichiometry of the trinuclear species was inverted, that is PdM_2,[4] Pt_2M,[5] or PtM_2[6, 7] compounds were formed with L acting as tridentate ligands (Scheme 1, c)).



Scheme 1. Different platinum coordination complexes.

We have now extended this work to heteronuclear complexes derived from the tetrakis(1-methylcytosine) complex $[Pt(1\text{-}MeC\text{-}N3)_4]^{2+}$ (**1**).[8] This starting compound is analogous to the previously described Pd^{II} compound,[9] but has the advantage of being more stable than the latter thereby increasing the chances for a successful preparation and isolation of heteronuclear derivatives. In a similar approach, Jitsukawa, Masuda, and co-workers have shown that $[PdL_4]^{2-}$ with L = DL-willardine[10] and L = 1-methyluracil[11] is capable of binding two alkali metal ions through the eight exocyclic carbonyl oxygens. The use of a starting compound containing cytosinato ligands, that is a ligand with different exocyclic groups (N and O), provides a unique opportunity to generate different donor sets for heterometal ions depending on the rotamer status of $[Pt(1\text{-}MeC\text{-}N3)_4]^{2+}$. Thus, cation **1** with its four cytosine bases arranged head-tail-head-tail (*htht*) provides two *trans*-N_2O_2 donor sets for two Cu^{II} ions and forms heteronuclear $Pt^{II}Cu^{II}_2$ species **2** which are extremely interesting as far as metal–metal interactions and magnetic properties are concerned. On the other hand, a second trinuclear compound **3** is reported, which displays an unusual head-head-head-head (*hhhh*) orientation of all four bases; this offers an N_4 donor set to Co^{III} and an O_4 donor set to Na^+, leading to the rare case of three different metal ions being bonded to the same nucleobase. Preliminary data on both trinuclear compounds **2** and **3** have been presented.[12]

Results and Discussion

Syntheses and spectroscopy of compounds: The CuPtCu compounds $[Pt(1\text{-}MeC^-\text{-}N3,N4,O2)_4Cu_2X_2]^{n+}$ (**2**) were prepared by reaction of $[Pt(1\text{-}MeC\text{-}N3)_4]^{2+}$ with a Cu^{II} salt in moderately basic (pH 8–12) aqueous solution and in part by subsequent substitution of X by other ligands. Compounds **2a** and **2b** were characterized by X-ray crystallography.

$[Pt(1\text{-}MeC^-\text{-}N3,N4,O2)_4Cu_2Cl_{1.6}(H_2O)_{0.4}](NO_3)_{0.4}\cdot 1.6\,H_2O$ **2a**

$[Pt(1\text{-}MeC^-\text{-}N3,N4,O2)_4Cu_2(H_2O)_2](NO_3)_2\cdot 3\,H_2O$ **2b**

Compounds with $X = NCS^-$ (**2c**) and N_3^- (**2d**) precipitated upon addition of KSCN and NaN_3, respectively, to aqueous solutions of **2a** or **2b**. The IR spectrum of **2c** ($\tilde{\nu}_{CN}$ 2097 cm^{-1}) suggests binding of the SCN^- ligand through N, since S coordination is expected to lead to a higher CN stretching frequency.[13] Formation of **2a** and **2b** occurs at a pH several log units below the estimated pK_a value (≈ 14) of the N3-platinated cytosine nucleobases and the free nucleobase (16.7),[14] respectively. Unexpectedly, compounds **2a**–**2d** are diamagnetic in solution, as they display sharp ^1H NMR resonances of the $1\text{-}MeC^-$ ligands. The spectrum of **2a** (D_2O, pD 8), for example, contains the cytosine H6 doublet at $\delta = 7.24$ ($^3J = 7.4$ Hz), the H5 doublet at $\delta = 5.14$, and the $N\text{-}CH_3$ singlet at 3.65. In comparison to the chemical shifts of **1**, H6 and H5 resonances are shifted upfield by 0.26 and 0.78 ppm, as expected for ligand deprotonation, whereas the CH_3 resonance is shifted downfield by 0.29 ppm. Acidification (pD 3, DNO_3) of the deep yellow solution of **2a** rapidly leads to the decomposition of the complex and reformation of **1**. UV/Vis spectra (H_2O) of **2a**–**2c** are virtually identical, with a weak band at 650 nm (ε 200 $LMol^{-1}cm^{-1}$) and a stronger one at 370 nm (ε 2500 $LMol^{-1}cm^{-1}$). The spectrum of **2d** displays minor differences (638 nm, 430 nm, 374 nm), which are possibly a result of an incomplete substitution of the X ligands of **2** by water in the case of X = azide.

Attempts to obtain mixed $Pt^{II}(Co^{II})_n$ complexes by reacting **1** with $Co(NO_3)_2$ at pH 12 were unsuccessful. The reaction takes place only in the presence of air or H_2O_2, which is evident in a color change from blue to brown. Red crystals of **3** were subsequently isolated in very low yield.

$[Pt(1\text{-}MeC^-)_4Co(H_2O)Na](NO_3)_2\cdot 2\,H_2O$ **3**

All attempts to improve the yield of **3** failed. The ^1H NMR spectrum of **3** in D_2O at pD 7.5 clearly reveals that the cytosine ligands are deprotonated (H6, $\delta = 6.97$, d, $^3J = 7.6$ Hz; H5, $\delta = 5.88$, d; CH_3, $\delta = 3.20$) and equivalent, and that the complex is diamagnetic. On the other hand, the protons of the $1\text{-}MeC^-$ rings are affected significantly differently from those of the CuPtCu compounds. The structure of **3**, as proven by X-ray crystallography (vide infra) is unique in that, unlike in **1**, the four 1-methylcytosinato ligands are arranged head-head-head-head (*hhhh*). ^1H NMR spectra of **1**[8] provide no evidence for any other rotamer being present in solution than the head–tail–head–tail (*htht*), which permits a maximum number of intramolecular hydrogen-bonding interactions. Since the tris(nucleobase) precursor of **1**, [Pt(1-MeC-

*N*3)$_3$Cl]$^+$ also adopts an *hth* conformation, the course of the formation of the all-head rotamer of **1** still remains unclear. Both an impurity of the *hhhh* rotamer in the bulk material of **1**, not detectable by ^{1}H NMR spectroscopy, and alternatively, ligand rotation under the influence of the coordinated heterometal ion seem possible.

Preliminary studies with other metal ions strongly suggest formation of related heteronuclear complexes. Thus reaction of $ZnCl_2$/NaOH and **1** in MeOH yields crystals of elemental composition **4** which, as a result of their extreme air-sensitivity (loss of solvent) and poor water solubility, were not further characterized.

$[Pt(1\text{-}MeC^-)_4Zn_2Cl_2]\cdot 2H_2O$ **4**

Upon heating in D_2O rapid reformation of **1** takes place. An excess of Hg^{II} salts (NO_3^-, ClO_4^-, $CF_3CO_2^-$, $CH_3CO_2^-$) leads to compounds with a stoichiometry close to $PtHg_4(1\text{-}MeC)_4$ (the protonation state of 1-MeC is unclear, possibly -2, anions omitted) which are formed at acidic pH 1–4. Obviously mercuration takes place also at the C5 position (H6 singlet at $\delta = 7.4$). We have previously observed mercuration reactions of N3-platinated 1-MeC, which occur at the N4 and C5 positions.[15]

X-ray crystal structures of 2a and 2b: Figures 1 and 2 provide different views of the cation of **2a**.

$[Pt(1\text{-}MeC^-\text{-}N3,N4,O2)_4Cu_2Cl_{1.6}(H_2O)_{0.4}](NO_3)_{0.4}\cdot 1.6H_2O$ **2a**

$[Pt(1\text{-}MeC^-\text{-}N3,N4,O2)_4Cu_2(H_2O)_2](NO_3)_2\cdot 3H_2O$ **2b**

The cation of **2b**, which possesses a crystallographic twofold axis passing through the Pt ion (dotted line in Figure 2), is qualitatively very similar and therefore not shown. Selected interatomic distances of **2a** and **2b** are listed in Table 1. The crystals of both compounds are formed by trinuclear $PtCu_2$ cations, nitrate anions, and disordered water molecules; the latter form a network of hydrogen bonds among themselves and with nitrate oxygens. As can be seen, the four cytosinato ligands, deprotonated at the N4 positions, are arranged *htht* like the four neutral bases in the starting compound **1**. The cations of **2a** and **2b** can formally be regarded as being built-up of an *htht*-$Pt(1\text{-}MeC^-)_4$ square-planar entity with two CuCl fragments in **2a** ($Cu(OH_2)$ in **2b**) added in such a way that the metals are inserted in the O_2N_2 donor sets above and below the Pt coordination plane. As a result of the metal centers being essentially collinear, the Cu-Pt-Cu angle is 178.58(3)° in **2a** and 179.31(10)° in **2b**. The two *trans*-positioned cytosinato

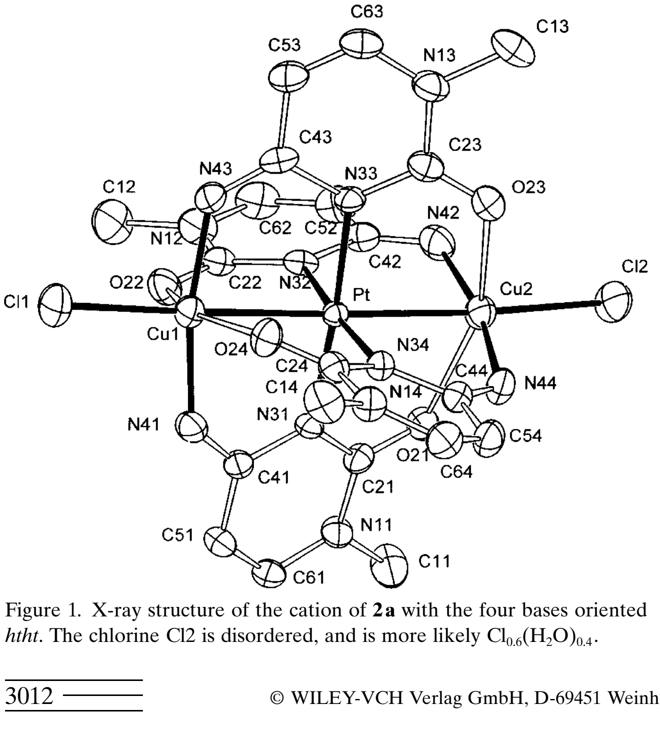


Figure 1. X-ray structure of the cation of **2a** with the four bases oriented *htht*. The chlorine Cl2 is disordered, and is more likely $Cl_{0.6}(H_2O)_{0.4}$.

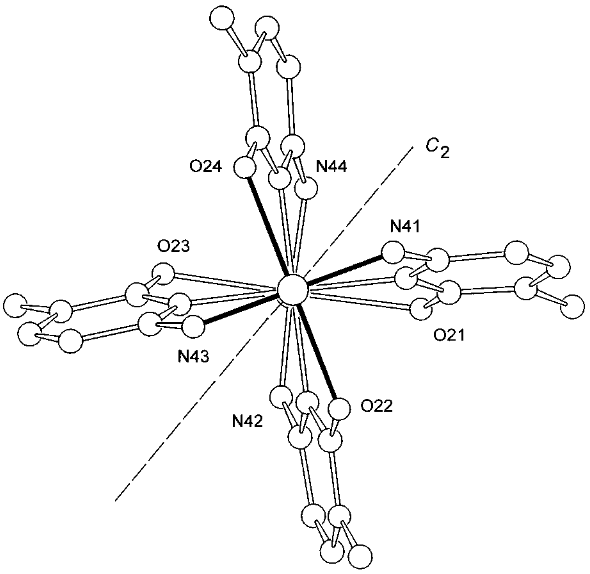


Figure 2. View of the $PtCu_2(1\text{-}MeC^-)_4$ portion of the cation of **2a** looking down the Cu1(black bonds)···Cu2 axis. The dotted line indicates the pseudo twofold axis in **2a**, and the crystallographic axis (through Pt) in **2b**.

Table 1. Selected bond lengths [Å] and angles [°] and geometrical parameters for **2a** and **2b**.

	2a (X = Cl)	**2b** (X = H_2O)[a]
Pt–N31, Pt–N34	2.034(5), 2.032(6)	2.031(11)
Pt–N32, Pt–N33	2.041(6), 2.046(5)	2.039(11)
Pt–Cu1, Pt–Cu2	2.531(2), 2.5272(14)	2.519(2)
Cu1–X1, Cu2–X2	2.304(3), 2.257(4)	2.070(12)
Cu1–N41, Cu2–N44	1.927(6), 1.904(7)	1.902(14)
Cu1–N43, Cu2–N42	1.910(7), 1.902(7)	1.89(2)
Cu1–O22, Cu2–O23	2.331(6), 2.341(6)	2.386(11)
Cu1–O24, Cu2–O21	2.413(6), 2.385(5)	2.302(11)
N31-Pt-N32, N33-Pt-N34	89.1(2), 90.5(2)	90.2(4)
N31-Pt-N33, N32-Pt-N34	174.8(2), 174.5(2)	175.9(5)
N31-Pt-N34	90.9(2)	89.0(6)
N32-Pt-N33	89.9(2)	90.8(6)
Cu1-Pt-Cu2	178.58(3)	179.31(10)
Pt-Cu1-X1, Pt-Cu2-X2	177.96(9), 174.66(12)	174.1(3)
N41-Cu1-N43, N42-Cu2-N44	168.1(3), 168.2(3)	169.9(7)
N41-Cu1-X1, N44-Cu2-X2	97.6(2), 95.8(2)	94.4(6)
N43-Cu1-X1, N42-Cu2-X2	94.3(2), 95.9(2)	95.6(7)
O23-Cu2-O21, O22-Cu1-O24	159.0(2), 158.6(2)	160.6(4)
2φ N4*-Cu···Cu-O2*	26.6(2), 28.1(3), 28.7(3), 29.4(3)	23.9(7), 25.4(7)
1/3, 2/4 bases [°][b]	29.9(3), 27.7(4)	23.6(8)

[a] In cation **2b**, with Pt located on a twofold axis, some geometrical parameters are equivalent through the symmetry operation $1 - x, y, \frac{1}{2} - z$. [b] angle between *trans* positioned 1-MeC$^-$ mean planes.

ligands are not coplanar but rather propeller-twisted. This feature can be confirmed by the "ideal" torsion angles O2-Cu ⋯Cu-N4 (2φ, see Table 1), and consequently the approximately planar and parallel CuO_2N_2, PtN_4, and CuO_2N_2 units are rotated with respect to each other by about φ.

The Pt^{II}–Cu^{II} distances are 2.531(2) and 2.527(1) Å in **2a**, and 2.519(2) Å in **2b**, and are therefore well within the range (2.49–2.56 Å) of those previously found in dinuclear PtCu complexes containing two *trans*-oriented 1-MeC^- ligands,[15] but considerably shorter than those in PtCu and Pt_2Cu compounds with two uracilato ligands in *cis*-orientation,[2b–2d] or in a Pt_2Cu complex with *trans*-oriented 2-pyridonato ligands.[3] These Pt–Cu distances are generally between 2.63[3] and 2.77 Å,[2d] although a distance of 2.98 Å was determined in a Pt_2Cu complex with crowded amine ligands at Pt.[2c] Assuming that the Pt–Cu distances correspond to bonding interactions (see below), Pt has a distorted octahedral coordination with four Pt–N3 equatorial distances in the range 2.031(11)–2.046(5) Å in both complexes. The $(N3)_4$ unit shows a slight tetrahedral distortion around Pt (±0.09 and ±0.08 Å in **2a**, and **2b**, respectively). The Cu coordination spheres consist of pairs of *trans*-oriented N4 and O2 donor atoms of 1-MeC^-, the Pt atom and the axial Cl/H_2O ligand. Inspection of interatomic distances reveals the following: i) The short Cu–N bonds (1.89(2)–1.927(6) Å) are comparable in length to those observed for heteronuclear PtCu complexes derived from *trans*-$a_2Pt(1\text{-}MeC\text{-}N3)_2]^{2+}$.[16] ii) In contrast, rather long distances between Cu and cytosinato O2 atoms (2.302(11)–2.413(6) Å) should be compared with those in a series of Pt_2Cu complexes with uracilato ligands (1.93–1.95 Å).[2b–2d] iii) The Cu–Cl (–OH_2) distances are close to the mean value of 2.274(33) Å (1.963(19) Å in the aqua derivative) reported as short distances in tetrahedrally distorted octahedral Cu^{II} complexes.[17] iv) Another distortion detectable in the Cu octahedrons is the significant bending of the O_2N_2 set towards Pt, which is characterized by the N4-Cu-N4 (168.1(3)–169.9(7)°) and O2-Cu-O2 angles (158.6(2)–160.6(4)°). These findings suggest that the unpaired electron at the Cu^{II} center is directed toward the Pt center and that this feature is important with respect to the unusual magnetic properties of these species (vide infra). On the basis of points ii) and iii), the octahedral Cu coordination polyhedron is elongated along the axial O⋯O direction, Pt being positioned in an equatorial position. This observation may have implications with respect to point iv).

It is worthwhile to compare the present structural features with those detected in the $[Cu_3(dpa)_4Cl_2]$ complex (dpa = bis(2-pyridyl)amide).[1g, 1h] The structure involves nearly linear Cl-Cu_3-Cl units, with the four dpa units acting as tridentate ligands, in an arrangement very similar to that found in **2a** and **2b**. However, the octahedrons around the two terminal Cu centers are elongated along the Cu-Cu-Cl direction, with long Cu–Cl distances of 2.465(1) Å.

X-ray crystal structure of 3: Figure 3 shows the structure of **3** in the crystal.

$[Pt(1\text{-}MeC^-\text{-}N3,N4,O2)_4Co(H_2O)Na](NO_3)_2 \cdot 2H_2O$ **3**

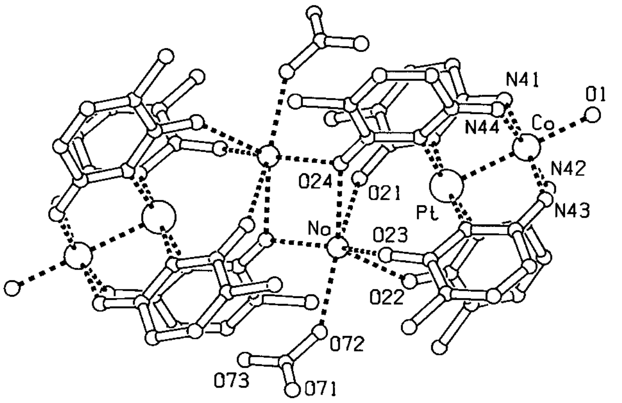


Figure 3. Centrosymmetric arrangement of pair of cations of **3**. Unlike **2a** and **2b** the four bases are arranged *hhhh*.

Table 2. Selected bond lengths [Å] and angles [°] for **3**.

Pt–N31	2.026(7)	Co–N41	1.904(9)
Pt–N32	1.992(9)	Co–N42	1.932(11)
Pt–N33	2.038(8)	Co–N43	1.915(9)
Pt–N34	1.994(10)	Co–N44	1.921(11)
Pt–Co	2.402(2)	Co–O1	1.975(9)
Pt⋯Na	3.369(5)		
N34-Pt-N32	176.8(4)	N41-Co-N42	89.4(4)
N34-Pt-N33	90.3(4)	N41-Co-N43	176.0(4)
N32-Pt-N33	90.1(4)	N41-Co-N44	90.2(4)
N34-Pt-N31	89.9(3)	N42-Co-N43	88.8(4)
N32-Pt-N31	89.5(4)	N42-Co-N44	174.9(4)
N33-Pt-N31	175.3(3)	N43-Co-N44	91.4(4)
Pt-Co-O1	179.3(3)	Co-Pt⋯Na	175.33(8)
φ N3*-Pt-Co-N4*	9.2(4), 9.3(3), 10.7(4), 9.5(3)		
1/3, 2/4 bases [°][a]	19.6(5), 21.3(4)		

[a] angle between *trans* 1-MeC^{-1} mean planes.

Selected interatomic distances are reported in Table 2. As pointed out above, formation of the *hhhh* conformation of the $Pt(1\text{-}MeC^-)_4$ moiety is yet unexplained. Complex **3** bears some resemblance to dinuclear, mixed-metal complexes derived from $[Pt(pytH)_4]^{2+}$ (pytH = pyridine-2-thiol),[18] even though Pt is bound through the exocyclic sulfur atom, and an *hhhh* arrangement certainly is sterically more easily achieved than in **1** with Pt binding to endocyclic N atoms of the four bases.

Unlike in **2a** and **2b** the heterometal Co^{III} in **3** is bound to the four deprotonated N4 sites of the 1-MeC^- ligands, to Pt (Pt-Co, 2.402(2) Å), and to what, on the basis of neutrality arguments and common sense, is assigned to a water molecule. Pt is surrounded by four N3 donor atoms, as in **1** as well as in **2a** and **2b**, and shifted by 0.069(4) Å from their mean plane away from cobalt. The cytosinato ligands around the metals are distorted in a propeller-twisted fashion, as in complexes **2a** and **2b**, and the torsion angle N3-Pt-Co-N4 (φ) is in the range 9.2(4)–10.7(4)°.

In the crystals, pairs of $Pt(1\text{-}MeC^-)_4Co$ units weakly bind two Na^+ ions through their sets of four O2 donors. Each sodium ion completes its distorted octahedral coordination sphere by an oxygen atom from a nitrate anion and an O2 atom of the other symmetry-related PtCo unit. The Na^+ ion is displaced from the plane of the four oxygen atoms by 1.2 Å away from Pt at a distance of 3.369(5) Å. All three metals are in an almost collinear arrangement (Na···Pt-Co angle of 175.33(8)°). The overall hexametallic unit is arranged about a crystallographic symmetry center as shown in Figure 3. The distance between symmetry-related Na^+ ions is 3.136(9) Å, while the Na···O distances and O···Na···O angles range between 2.330(10) and 2.694(9) Å and between 68.2(3) and 158.3(4)°, respectively. Compound **3** is only the second example of a structurally characterized nucleobase complex containing three different metals associated with a single nucleobase; the other example we are aware of is $[\{Pt(NH_3)_2(1\text{-}MeU)_2\}_2AgNa(H_2O)_4](ClO_4)_2\cdot 6.5\,H_2O$ (1-MeU = 1-methyluracilate).[19]

Magnetic properties of 2a and 2b: Magnetic susceptibility data for **2a** and **2b** were collected in the temperature range 2–295 K with a SQUID magnetometer in an applied external field of 1 T (**2a**) and 5 T (**2b**). In Figure 4 the effective magnetic moments μ_{eff} as a function of temperature are shown for the two compounds studied. μ_{eff} decreases with decreasing temperature from 0.54 μ_B at 295 K to 0.24 μ_B at ~150 K (**2a**) and from 0.48 μ_B at 295 K to 0.20 μ_B at ~160 K (**2b**).

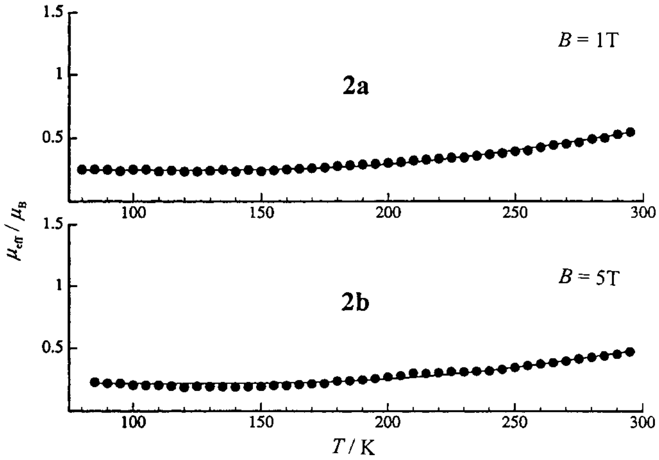


Figure 4. Temperature dependence of the magnetic moments for complexes **2a** and **2b**. The solid lines represent the best least-squares fits of the experimental data to the HDvV model.

The two Cu^{II} ions strongly couple ($J = 980 \pm 30\ cm^{-1}$ (**2a**) and $1030 \pm 30\ cm^{-1}$ (**2b**)) in an antiparallel fashion, leading to diamagnetism below ~150 K (ground state $S_t = 0$). The magnetic moment measured below ~150 K is attributed to a paramagnetic impurity of Cu^{II} (2% (**2a**); 1.6% (**2b**)). Experimental data were fitted with the Heisenberg–Dirac–van Vleck (HDvV) spin Hamiltonian [Eq. (1)].

$$H = \sum_{i,j=1;\, i<j}^{n} J_{ij}\vec{S}_i\cdot\vec{S}_j \qquad (1)$$

For the trinuclear compounds with the paramagnetic Cu^{II} ions ($S_1 = S_3 = ½$) and the central diamagnetic Pt^{II} ion ($S_2 =$ O), Equation (1) gives $H = J_{13}\vec{S_1}\cdot\vec{S_3} = J\vec{S_1}\cdot\vec{S_3}$. The temperature-dependent magnetic moments in Figure 4 are corrected for the diamagnetic contribution of the holder and the sample ($\chi_D = -397\times10^{-6}\ cm^3mol^{-1}$ (**2a**) and $-440\times10^{-6}\ cm^3mol^{-1}$ (**2b**)) and for temperature independent paramagnetism (TIP $\approx +178\times10^{-6}\ cm^3mol^{-1}$ (**2a**) and $+163\times10^{-6}\ cm^3mol^{-1}$ (**2b**)). This TIP represents the sum of the individual TIP values for Cu (ca. $+60\times10^{-6}\ cm^3mol^{-1}$)[20] and Pt (ca. $+58\times10^{-6}\ cm^3mol^{-1}$ (**2a**); ca. $+43\times10^{-6}\ cm^3mol^{-1}$ (**2b**)). It is well established that $5d^8$ complexes have only small TIP values.[21] For the fitting procedure an isotropic g value for Cu^{II} of 2.2 was applied.[22–24]

Strong exchange interactions in di- and trinuclear Cu^{II} complexes are known from the literature,[25–29] even for distances as large as 15.6 Å, but J values of approximately $1000\ cm^{-1}$, as observed for **2a** and **2b**, have not been reported. However, from the temperature dependence of the magnetic susceptibility of an azido-bridged Cu_2 compound reported in the literature,[29] it would seem that a similar or even larger J value as in **2a** and **2b** is feasible. Incidentally, the Cu–Cu distance in this compound is rather similar (5.145(1) Å) to that in **2a** and **2b**.

Analysis of Pt–Cu interactions in 2a, 2b, and related nucleobase compounds: The strong chelating power of the nucleobases certainly helps to bind two and three electron-rich metal atoms together on one axis. Nevertheless, attractive electronic factors must overcome the repulsions, especially those between the axial lone pairs of the metals. For d^8–d^8 or d^8–d^{10} dimers with L_4M or L_2M components (also stable as isolated square-planar and linear monomers with 16 or 14 electrons, respectively), we previously described the M–M′ interaction as in **I** (Figure 5). At first glance, four electrons in the z^2-type orbitals and none in the p_z orbitals could only suggest an M–M′ repulsion. However, the lack of specular symmetry through the metals allows the mixing of noded (p_z) and unnoded (z^2 and s) atomic orbitals. The rehybridization of the populated σ and σ* MOs altogether permits a weak M–M′ attraction. Also, the more expanded, protruding lobes of the HOMO (σ*) are repulsive toward incoming axial ligands so that the L_4M–$M'L_3$ structural motif is only attained by discarding one or two electrons (d^8–d^9 and d^8–d^8 systems).[30] The M–M′ distance decreases according to the progressive depopulation of the M–M′ σ* level.

Although characterized by a filled z^2 orbital, a second L_2M (d^{10}) unit can add up to a d^8–d^{10} dimer as found in the structure of the d^{10}–d^8–d^{10} trimer $Au_2Pt(CH_2P(S)Ph_2)_4$.[31] The calculated Au–Pt overlap population is larger than in the dimeric precursor because of the more effective involvement of the metal p_z orbitals, imposed by symmetry. In fact, as shown in Figure 5 (**II**), while the central p_z orbital receives electrons from the σ* combination of lateral z^2 orbitals, backdonation occurs from the central z^2 orbital into the in-phase combination of lateral p_z orbitals. Essentially, two distinguished delocalized interactions involving two pairs confer single bond orders to the two M–M′ linkages. The latter are obviously contrasted by the repulsion amongst the z^2 orbitals which are all filled (b., n.b., and a.b.). As for the dimer, addition of coaxial σ donor ligands requires electron loss from the HOMO (a.b.). Thus for the mentioned Au_2Pt trimer, a Cl_2 molecule adds oxidatively giving rise to species $L_3AuPtL_4AuL_3$ with a formal $d^9d^8d^9$ electron count. The structural characterization of both species indicates a decrease of the Pt–Au distances from 3.034 to 2.666 Å.[31]

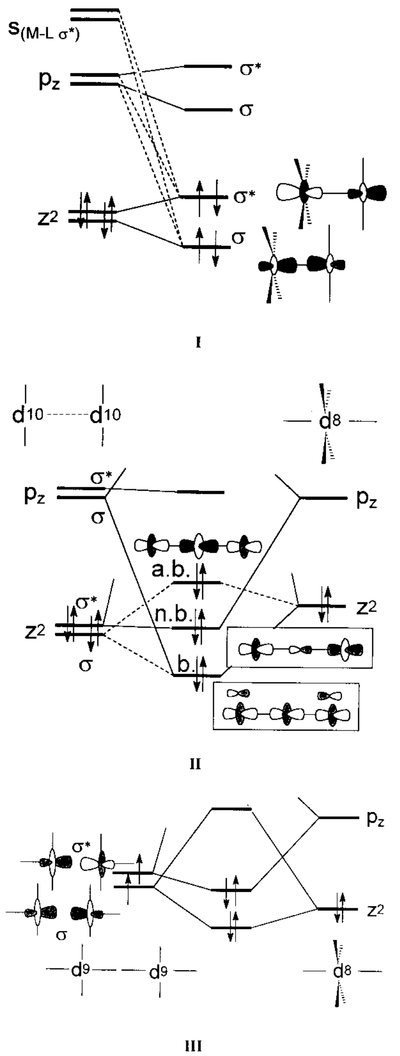


Figure 5. Molecular orbital diagrams for bimetallic d^8-d^8 system (**I**), for $d^{10}-d^8-d^{10}$ (**II**), and $d^9-d^8-d^9$ trimers (**III**).

The latter Au_2Pt system is fully analogous to the present Cu_2Pt trimers **2a** and **2b**, which are obtained directly from Pt^{II} and Cu^{II} species and which contain terminally bound ligands. Again, the M–M distances are significantly shorter by a few decimal units than those of the dimeric species (d^8-d^9). In the T-shaped terminal fragments, the previously distinct z^2 and p_z orbitals, are largely mixed (**III**, Figure 5). Simplified, the p_z orbitals are used for bonding the terminal ligands, while the z^2 orbitals (recalled as the x^2-y^2 type) are hybridized with p_z to point inwards. The distal d^9-d^9 L_3M fragments can couple their unpaired spin through both the interaction of latter hybrids with the central p_z and z^2 orbitals. Two M–M single bonds are again featured with the advantage that the contrasting repulsion is eliminated by the vacancy at the antibonding level. Ultimately, the effect of terminal donors is also an increase in the HOMO–LUMO gap. On the other hand, it cannot be excluded that, for an appropriate combination of metals and ligands, two electrons could be also dismissed from **II**, thus stabilizing a $d^9-d^8-d^9$ trimer of the type $L_2M-M'L_4-ML_2$. If the latter electron count relieves the repulsion between the aligned z^2 orbitals, a good percentage of M–M bonding continues to stem from the already effective donation of the terminal z^2-filled orbitals into the empty p_z orbital of the central metal atom. Such a qualitative viewpoint seems quite general and we see no reason to deny the latter bonding contribution also in trimers formed upon stacking of trigonally planar Cu^I units. It is worth mentioning that the interpretaion given to recent DFT calculations[32] is such to exclude any direct Cu–Cu bonding in $Cu_3[(p\text{-tol})N_5(p\text{-tol})]_3$ in spite of the shortest Cu^I–Cu^I separations ever observed experimentally.[33]

As cited above,[30] the four-electron repulsion resulting from two square-planar d^8-d^8 systems, can formally be used to describe the linkage in the PtCo dimer (d^8-d^6 system). In fact, by subtracting two electrons, the main interaction between the Pt square-planar and the square-pyramidal fragments is of the type two electrons/two orbitals; this suggests a donor–acceptor (i.e., dative) Pt→Co bond with an overlap population of 0.240 as the formal bond order that would correspond to a Pt^{II}–Co^{III} distance of 2.40 Å. By taking into account the isolobal analogy between FMOs,[34] we can rationalize this bonding pattern to other homo- and heterobimetallic complexes with or without nucleobases.[30]

Figure 6 illustrates the efficient conditions in L_4Pt-ML_n systems (number of ligands $n=5$, 3, 1, and electrons in the ML_n fragment) to produce a dative bond. The latter case applies to organometallic complexes without bridging ligands, such as the 4:1 type $[R_4Pt^{II}Ag^{I}X]^-$ ion (R = perhalophenyl, X = neutral ligand), where a Pt→Ag dative bond of about 2.65 Å has been reported.[35]

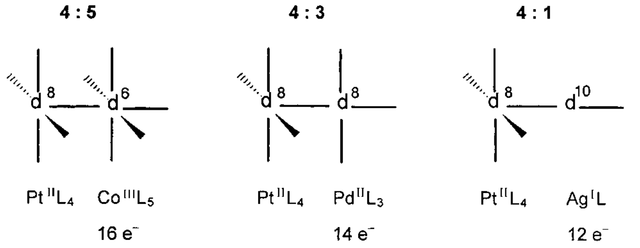


Figure 6. Number of ligands and electrons at the ML_n fragment to allow a dative bond in L_4Pt-ML_n systems.

Conclusion

Tridentate ligands containing three appropriately spaced N donor atoms (N′,N,N′) such as the anion of bis(2-pyridyl)-amine (dpa) have been instrumental in the development of homonuclear M_3 linear chain compounds.[1] Cyclic imide ligands with an O,N,O donor sequence are equally suitable for the preparation of linear chain heteronuclear compounds and examples of MPtM compounds (M = alkali ion) have been reported.[10, 11] Herein, we have described the use of unsymmetrical 1-methylcytosinato ligands, which provide N′,N,O (N′ = N4, N = N3, O = O2) donor sets and can be applied to generate heteronuclear MPtM or MPtM′ compounds, depending on the rotamer status of the starting compound $[Pt(1\text{-MeC-}N3)_4]^{2+}$ (**1**). When the heterometals are present in their (preferred) *htht* arrangement, they are offered two identical *trans*-N'_2O_2 donor sets at either side of the Pt. This set, combined with the spatial disposition of the donor atoms, appears to be crucial in forcing the Cu^{II} ions in **2** to direct their half-filled d orbitals towards the central Pt^{II} ion with the latter as a mediater for exchange interaction. On the other hand, if the four nucleobases of **1** adopt the (rare) *hhhh* arrangement, two different ligand sets, N'_4 and O_4, are generated which as expected will not favor formation of a heteronuclear MPtM compound but rather will differentiate heterometal ions by their preference for respective donor sets. Consequently, in **3** a Co^{III} ion binds to the four N′ sites, whereas the hard Na^+ ion attaches itself to the O_4 set. There are, in principle, two more configurations of heterometal binding sets possible with **1**: two *cis*-N'_2O_2 as well as N'_3O and O_3N'sites.

The *hhtt* and *hhht* rotamers would provide two *cis*-N'_2O_2 as well as N'_3O and O_3N' donor sets, respectively, but it may be difficult to prepare these rotamers. However, combining cytosine and other nucleobases in mixed-ligand complexes of type $[PtB_xB'_y]^{n+}$ $(x + y = 4)$ may be another route to generate nonidentical binding sites for heterometal ions in linear chain compounds. Compounds of type $[Pt(1\text{-MeC-}N3)_3(\text{pu-}N7)]^{2+}$ (with pu = 9-methyladenine and 9-ethylguanine) have in fact been prepared, yet with a different aim from the one raised herein.[36]

Experimental Section

Materials: $[Pt(1\text{-MeC-}N3)_4](NO_3)_2$ (**1**)[8] (from K_2PtCl_4 and 1-MeC[37]) was synthesized according to the literature. For the synthesis of the other complexes, see below. All other materials (pro analysis) used in the experiments were purchased from Merck, Darmstadt (Germany).

Instrumentation: ^1H NMR spectra (D_2O) were recorded at ambient temperature on a Bruker AC200 spectrometer. Chemical shifts were measured with internal reference to sodium-3-(trimethylsilyl)propanesulfonate. pD values were determined with a glass electrode (Sigma – Aldrich) on a Metrohm 632 pH meter by adding 0.4 units to the meter reading. IR spectra (KBr) were taken on a Bruker IFS28 FT spectrometer. UV/Vis spectra were recorded on a Perkin – Elmer Lambda 15 instrument with cuvettes of 1 cm diameter. Elemental analyses were carried out on a LECO Elemental Analyzer CHNS-932 or a Carlo Erba Strumentazione 1106 instrument. Electron probe X-ray microanalysis (EPXMA) was performed on a Cambridge Instruments Stereoscan 360 instrument. Magnetic measurements were performed with a SQUID magnetometer (MPMS) from Quantum Design.

X-ray diffraction studies: Diffraction data for **2a** and **3** were collected at 293 K with an Enraf – Nonius CAD4 single crystal diffractometer equipped with graphite monochromator and $Mo_{K\alpha}$ radiation. Unit cell dimensions for both structures were determined from 25 reflections in the range 13.5 – 18.5°. Reflections were corrected for Lorentz and polarization effects and absorption through an empirical ψ scan method. Diffraction data of **2b** were collected at room temperature on an Enraf – Nonius – Kappa CCD[38] ($Mo_{K\alpha}$, $\lambda = 0.71069$ Å, graphite-monochromator) with a sample-to-detector distance of 26.7 mm. They covered the whole sphere of reciprocal space by measurement of 360 frames rotating about ω in steps of 1° with a scan time of 20 s per frame. Preliminary orientation matrices and unit cell parameters were obtained from the peaks of the first ten frames, and refined with the whole data set. Frames were integrated and corrected for Lorentz and polarization effects with DENZO.[39] The scaling as well as the global refinement of crystal parameters was performed by SCALEPACK.[39] Reflections, which were partly measured on previous and following frames, are used to scale these frames on each other. This procedure in part eliminates absorption effects and also considers any crystal decay.

All structures were solved by standard Patterson methods[40] and refined by full-matrix least-squares based on F_o^2 with the SHELXTL-PLUS[41] and SHELXL 93 programs.[42] The scattering factors for the atoms were those given in the SHELXTL-PLUS program. All non-hydrogen atoms have been refined anisotropically with the following exceptions: The disordered nitrate anion (occupancy ~0.40) and four water molecules with half occupancy in **2a**, and the atoms of the two half-occupied nitrate anions and the three half-occupied water molecules in **2b**. In compound **2a**, the presence in the ΔF map of a poorly defined NO_3^- ion and the high thermal parameter observed for Cl2 led us to refine the occupancy factors (which must be added to unit for neutrality reasons) of the NO_3^-/Cl groups. The final values were 0.41(4)/0.59(4) neglecting any contribution of a possible water ligand in the position of the chlorine. Hydrogen atoms were placed at calculated positions except for the amino protons, which could be localized with difference fourier synthesis, and were refined with a common isotropic temperature factor. The high *R* factors for **3** are a result of the poor quality of the crystals available and the residual peaks in a void (probably from solvent molecules). Attempts to refine these were unsuccessful. Crystallographic data and experimental details are reported in Table 3. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-120194 – 120196. Copies of the data can be obtained free of charge on an application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223336-033; e-mail: deposit@ccdc.cam.ac.uk).

Preparation of $[Pt(1\text{-MeC}^-)_4Cu_2Cl_{1.6}(H_2O)_{0.4}](NO_3)_{0.4} \cdot 1.6\,H_2O$ (2a): The pH of a solution of **1** (205 mg, 0.25 mmol) and $CuCl_2 \cdot 2\,H_2O$ (128 mg, 0.75 mmol) in H_2O (10 mL) was adjusted to 12 with NaOH. The mixture

Table 3. Crystal data and structure refinement of compounds **2a**, **2b**, and **3**.

Compound	**2a**	**2b**	**3**
formula	$C_{20}H_{28}Cl_{1.6}Cu_2N_{12.4}O_{7.2}Pt$	$C_{20}H_{34}Cu_2N_{14}O_{15}Pt$	$C_{20}H_{30}CoN_{14}NaO_{13}Pt$
M_r [g mol^{-1}]	936.56	1032.78	951.59
crystal system	triclinic	monoclinic	triclinic
space group	$P\bar{1}$ (no 2)	$C2/c$ (no 15)	$P\bar{1}$ (no 2)
a [Å]	11.697(4)	13.938(3)	12.161(5)
b [Å]	13.000(5)	20.266(4)	12.364(3)
c [Å]	13.315(5)	12.929(3)	12.846(6)
α [°]	90.73(3)		117.60(3)
β [°]	116.04(2)	100.22(3)	111.83(4)
γ [°]	116.20(2)		90.87(3)
V [Å^3]	1577.6(10)	3594.1(13)	1547.2(10)
Z	2	4	2
ρ_{calc} [Mg m^{-3}]	1.972	1.909	2.043
μ [mm^{-1}]	5.953	5.139	5.154
$F(000)$	912	2032	936
θ range for data collection	1.76 – 26.98	4.57 – 25.60	2.05 – 27.98
h, k, l ranges	− 14/12, − 16/16, 0/16	− 13/16, − 24/13, − 15/15	− 16/14, − 16/14, 0/16
reflns collected	6942	4686	7299
unique reflns	6857	3106	6976
R(int)	0.0219	0.0495	0.0325
observed [$I > 2\sigma(I)$]	5612	2060	4625
refined parameters	407	242	455
goodness-of-fit	1.047	1.084	1.152
extinction coeff.	–	0.0005(2)	–
$R1$	0.0421	0.0412	0.0577
$wR2$	0.1195	0.0926	0.1435
residuals [e Å^{-3}]	1.922, − 2.036	1.007, − 0.595	2.512,[a] − 2.923

[a] located near Pt ion.

was stirred at ambient temperature for three days. The green precipitate was filtered off. The solvent of the resulting clear yellow solution was allowed to evaporate at 4°C. After four weeks dark-brown plates of **2a** (51.5 mg, 22%) were collected. $C_{20}H_{28}N_{12.4}O_{7.2}Cl_{1.6}Cu_2Pt$ (936.21): calcd C 25.7, H 3.0, N 18.6, Cl 6.1; found C 25.4, H 3.0, N 19.1, Cl 5.8; IR (KBr): $\tilde{\nu}$ = 3439, 3296, 2923, 1650, 1565, 1483, 1395, 1290, 807, 766, 625 cm^{-1}.

Preparation of $[Pt(1\text{-}MeC^-)_4Cu_2(H_2O)_2](NO_3)_2 \cdot 3H_2O$ (2b): A solution of **2a** (94 mg, 0.10 mmol) and $AgNO_3$ (27 mg, 0.16 mmol) in H_2O (40 mL) was stirred for three days with exclusion of light. After AgCl was filtered off, the resulting solution was concentrated to 5 mL by rotary evaporation. Subsequent evaporation at 4°C gave dark-brown crystals of **2b** (83.2 mg, 85%). $C_{20}H_{28}N_{14}O_{12}Cu_2Pt$ (978.70): calcd C 24.5, H 2.9, N 20.0; found C 24.4, H 2.9, N 20.0; IR (KBr): $\tilde{\nu}$ = 3437, 2922, 1651, 1567, 1485, 1385, 1295, 808, 767, 628 cm^{-1}.

Preparation of $[Pt(1\text{-}MeC^-)_4Cu_2(NCS)_2] \cdot 2.5H_2O$ (2c): KSCN (24 mg, 0.25 mmol) was added to a stirred solution of **2a** (47 mg, 0.05 mmol) in H_2O (35 mL, pH 10–11). Within few minutes the color of the solution turned from dark-yellow to green. Upon standing a light-green precipitate of **2c** (26.5 mg, 54%) appeared, which was filtered off and washed with H_2O (5 mL). $C_{22}H_{29}N_{14}O_{6.5}S_2Cu_2Pt$ (979.85): calcd C 27.0, H 3.0, N 20.0; found C 26.9, H 2.7, N 20.0; IR (KBr): $\tilde{\nu}$ = 3450, 3302, 2922, 2097, 1655, 1570, 1485, 1295, 796, 766, 626 cm^{-1}.

Preparation of $[Pt(1\text{-}MeC^-)_4Cu_2(N_3)_2] \cdot 2H_2O$ (2d): Compound **2a** (28.1 mg, 0.03 mmol) was dissolved in H_2O (10 mL) and NaN_3 (5.9 mg, 0.09 mmol) was added upon stirring. Then the mixture was cooled to 4°C. After two hours a dark-green precipitate of **2d** (20.6 mg, 73%) was filtered off and washed with H_2O (5 mL). $C_{20}H_{28}N_{18}O_6Cu_2Pt$ (938.73): calcd C 25.6, H 3.0, N 26.9; found C 25.6, H 2.8, N 27.0; IR (KBr): $\tilde{\nu}$ = 3433, 2921, 2036, 1653, 1562, 1490, 1292, 799, 765 cm^{-1}.

Preparation of $[Pt(1\text{-}MeC^-)_4Co(H_2O)Na](NO_3)_2 \cdot 2H_2O$ (3): Compound **1** (328 mg, 0.4 mmol) and $Co(NO_3)_2 \cdot 6H_2O$ (466 mg, 1.6 mmol) were dissolved in H_2O (30 mL). An aqueous H_2O_2 solution was added (10%, 800 μL) and the pH was adjusted to 12 by addition of NaOH. The mixture was stirred for three days at room temperature. A brown precipitate, presumably $Co(OH)_3$ (IR), was filtered off and the resulting yellow filtrate was concentrated to 10 mL by rotary evaporation. Slow crystallization of the filtrate at 4°C led to the formation of red crystals of **3** in approximately 1% yield. Compound **3** was characterized by ^1H NMR spectroscopy, X-ray crystallography (see above), as well as electron probe X-ray microanalysis and IR spectroscopy. EPXMA gave a Pt:Co:Na ratio of 1:1:1. IR (KBr): $\tilde{\nu}$ = 3439, 3278, 3211, 2919, 1663, 1588, 1441, 1384, 1335, 1298, 808, 764, 640 cm^{-1}.

Preparation of $[Pt(1\text{-}MeC^-)_2Zn_2Cl_2] \cdot 2H_2O$ (4): **1** (82 mg, 0.1 mmol) and $ZnCl_2$ (27 mg, 0.2 mmol) were dissolved in MeOH (40 mL). NaOH (16 mg, 0.4 mmol) dissolved in MeOH (5 mL), was added and the mixture was cooled to 4°C. Within several hours colorless needles of **4** (43.7 mg, 47%) precipitated, which were very air-sensitive. $C_{20}H_{28}N_{12}O_6Cl_2Zn_2Pt$ (929.26): calcd C 25.9, H 3.0, N 18.1; found C 25.7, H 3.0, N 18.1; IR (KBr): $\tilde{\nu}$ = 3440, 3298, 2924, 1657, 1615, 1566, 1482, 1439, 1396, 1299, 803, 769, 616 cm^{-1}; Raman (solid state): $\tilde{\nu}$ = 3297, 3089, 2954, 1663, 1618, 1550, 1529, 1344, 1304, 1229, 812, 655, 624 cm^{-1}.

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