DALTON

Cytosine nucleobase as a tridentate ligand: Metal binding to N^3, N^4 and O^2 in the trinuclear complex *cis*-$[Pt(NH_3)_2(mcyt)_2\{Pd(en)\}_2][NO_3]_4\cdot H_2O$ (mcyt = 1-methylcytosinate, en = ethane-1,2-diamine)

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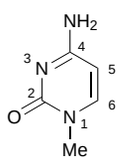
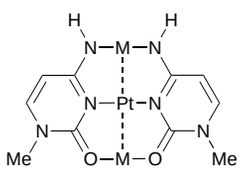
The reaction of *cis*-$[Pt(NH_3)_2(Hmcyt\text{-}N^3)_2][NO_3]_2$ with $[Pd(en)(H_2O)_2][NO_3]_2$ (Hmcyt = 1-methylcytosine; en = ethane-1,2-diamine) yielded the trinuclear complex *cis*-$[Pt(NH_3)_2(mcyt\text{-}N^3,N^4,O^2)_2\{Pd(en)\}_2][NO_3]_4\cdot H_2O$, in which the anionic 1-methylcytosinato ligands (mcyt) adopt a head-to-tail arrangement, with Pt co-ordinated to N^3 of two mcyt nucleobases, and both Pd metal ions having a mixed N^4,O^2 donor set. Crystal data: orthorhombic, space group *Pbcn*, $a = 20.903(2)$, $b = 13.510(1)$, $c = 12.024(1)$ Å, $U = 3395.5(9)$ Å^3, $Z = 4$. The Pt · · · Pd distances within the trinuclear cation are 2.9365(6) Å.

N^1-Substituted cytosine nucleobases display rather versatile metal-ion binding patterns.[1] Metal binding has been established for N^3, N^4, O^2, C^5 and combinations thereof, *e.g.* N^3/O^2 or N^3/N^4 or $N^3/N^4/N^4$.[2] Recently, we have observed two novel tridentate binding patterns, through N^3,N^4,O^2 (ref. 3) and *via* N^3,N^4,C^5.[4] In both cases, two N^3 positions of a cytosine nucleobase [1,5-dimethylcytosine (Hdmcyt)[3] or 1-methylcytosine (Hmcyt)[4]] are cross-linked by a *trans*-$Pt^{II}(NH_2Me)_2$ entity and heterometal ions are successively added to pairs of N^4 nitrogens, O^2 oxygens and C^5 carbons, respectively **a** and **b**. Probably because deprotonated N^4 is a better donor than O^2 and because of easy rotation of the cytosine nucleobase about the Pt–N^3 bonds in *trans*-$Pt^{II}(NH_2Me)_2$ complexes,[5] in no instance has a mixed N^4,O^2 binding scheme of a heterometal ion been observed, not in any dinuclear nor in the trinuclear compounds.

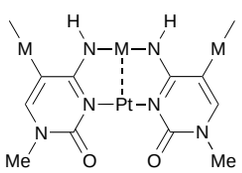
Cytosine rotation about the Pt–N^3 bond is, however, considerably more difficult in the case of *cis*-$[Pt(NH_2Me)_2(Hmcyt)_2]^{2+}$ due to steric crowding[6,7] and that is why we considered chelation of a second metal ion through N^4 of one cytosine nucleobase and O^2 of the other one feasible. We have now realized such a possibility. Thus, reaction of *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$ with $[Pd(en)(H_2O)_2]^{2+}$ (en = ethane-1,2-diamine) leads to formation of the trinuclear compound *cis*-$[Pt(NH_3)_2(mcyt)_2\{Pd(en)\}_2][NO_3]_4$ which was detected in solution and crystallized as a monohydrate (**c**).



Hmcyt



a



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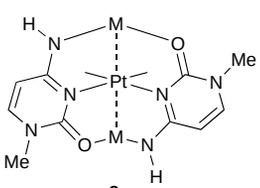


c

Experimental

Preparation of *cis*-$[Pt(NH_3)_2(mcyt)_2\{Pd(en)\}_2][NO_3]_4\cdot H_2O$

To a solution of $[Pd(en)(H_2O)_2][NO_3]_2$ (9.264 mmol) in water (10 cm^3), prepared from $Pd(en)Cl_2$ and $AgNO_3$ (2 equivalents) and filtration to remove AgCl, was added *cis*-$[Pt(NH_3)_2(Hmcyt)_2][NO_3]_2$ (0.131 mmol)[8] and the pH of the light yellow solution adjusted to 5 by means of 1 M NaOH. Slow evaporation at 40 °C yielded dark orange crystals of the required compound, admixed with starting material. Recrystallization from water gave *cis*-$[Pt(NH_3)_2(mcyt)_2\{Pd(en)\}_2][NO_3]_4\cdot H_2O$ in 26% yield (Found: C, 15.1; H, 3.4; N, 20.5. Calc. for $C_{14}H_{36}N_{16}O_{15}Pd_2Pt$: C, 15.6; H, 3.4; N, 20.8). ^{1}H NMR (δ, D_2O): 6.88 (H^6, d, ^3J 7.5 Hz), 5.66 (H^5, d), 3.24 (CH_3, s), 2.79 (en, m).

Proton NMR studies

Proton NMR spectra were recorded on Bruker AC200 and DRX400 FT spectrometers in D_2O solutions containing sodium 3,3,3-trimethylpropanesulfonate as internal reference. Values of pD (D_2O solutions) were determined by use of a glass electrode and addition of 0.4 units to the meter reading.[9] Aqua species of *trans*-$Pd(NH_3)_2Cl_2$[10] and *cis*-$Pt(NH_3)_2Cl_2$[11] were prepared by treating the chloro complexes with $AgNO_3$ (2 equivalents) in D_2O and filtering off or centrifuging off the AgCl, depending on the scale of the experiment, following cooling of the samples on ice. In a typical experiment, *cis*-$Pt(NH_3)_2Cl_2$ (30 mg, 0.1 mmol) and $AgNO_3$ (33.2 mg, 0.2 mmol) were mixed in D_2O (1 ml), the mixture stirred at 40 °C for 3 h, then kept at 0 °C for 2 h, and finally centrifuged from AgCl. The equivalent amount of *cis*-$[Pt(NH_3)_2(Hmcyt)_2][NO_3]_2$ was added to 0.5 ml of this solution and, with or without pD adjustment, the reaction was followed by ^{1}H NMR spectroscopy.

X-Ray crystallography

A crystal of *cis*-$[Pt(NH_3)_2(mcyt\text{-}N^3,N^4,O^2)_2\{Pd(en)\}_2][NO_3]_4\cdot H_2O$ of approximate dimensions 0.20 × 0.15 × 0.40 mm was used for the X-ray analysis. $C_{14}H_{34}N_{16}O_{14}Pd_2Pt\cdot H_2O$, $M = 1076.43$, orthorhombic, space group *Pbcn* (no. 60), $a = 20.903(2)$, $b = 13.510(1)$, $c = 12.024(1)$ Å, $U = 3395.5(9)$ Å^3, $Z = 4$, $D_c = 2.11$ g cm^{-3}, μ(Mo-Kα) = 52.63 cm^{-1}, $F(000) = 2008$.

Unit-cell dimensions were determined from Weissenberg photographs, later refined by least-squares treatment of 25 reflections in the range θ 14–17°. A total of 5472 reflections were collected (Enraf-Nonius CAD4, graphite monochromator,

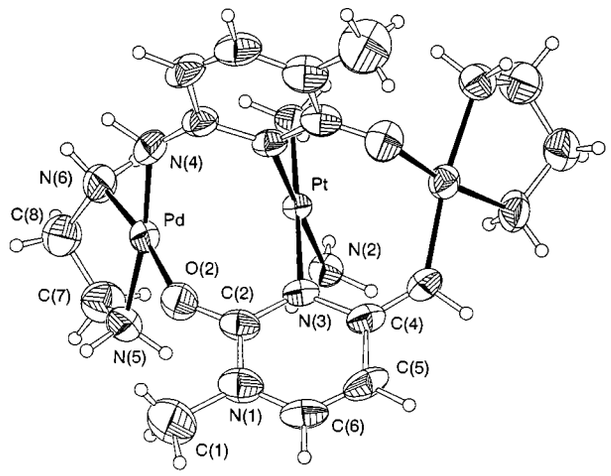


Fig. 1 An ORTEP[15] drawing of the cation *cis*-$[Pt(NH_3)_2(mcyt\text{-}N^3,N^4,\text{-}O^2)_2\{Pd(en)\}_2]^{4+}$ with 40% probability thermal ellipsoids. The Pt ion is located on a two-fold crystallographic axis, bisecting the N(3)–Pt–N(3′) angle. The numbering scheme refers to atoms of the crystallographically independent moiety

Mo-Kα radiation, $\lambda = 0.710\ 73$ Å, room temperature, $2\theta_{max} = 60°$, $+h$, $+k$, $+l$), later corrected for Lorentz-polarization effects and absorption (empirical ψ-scan method, $\%T$ min and max = 92.0, 99.9). Three standard reflections, measured at regular intervals throughout the data collection, showed no noticeable variation in intensity.

The structure was solved by conventional Patterson and Fourier techniques and refined on F by full-matrix anisotropic least-squares methods using 3006 reflections with intensities $I \geqslant 3\sigma(I)$. After anisotropic refinements, the calculated positions of the hydrogen atoms all occurred in positive electron density regions. A Fourier-difference synthesis revealed the presence of two water molecules (occupancy 0.25 each, on the basis of the respective electron density peaks). The final cycles with fixed contributions from the hydrogen atoms ($B = 1.3 \times B_{eq}$ of their bonded atom), except those of the solvent molecules, converged to final $R(F) = 0.035$, $R'(F) = 0.038$, for 220 parameters. Weighting scheme $1/\sigma(F)^2$, goodness of fit 1.33, maximum positive and negative peaks in ΔF map 0.81 and −0.99 e Å^{-3}, respectively. Atomic scattering factors and anomalous dispersion parameters were taken from ref. 12. All calculations were carried out using the Enraf-Nonius MOLEN package[13] on a Micro VAX2000 computer.

CCDC reference number 186/697.

Results and Discussion

Formation and X-ray analysis

Reaction of *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$ with $[Pd(en)(D_2O)_2]^{2+}$ was initially studied by ^{1}H NMR spectroscopy. Reaction was evident from a drop in pD, a colour change from light yellow to orange, and the appearance of new cytosine resonances. Thus, new H^5 and H^6 cytosine doublets upfield from those of the starting compounds [H^6, Δδ 0.67 ppm; H^5, Δδ 0.3 ppm], emerge. Only single sets of new resonances are observed, thereby confirming the presence of two chemically equivalent cytosine rings in the product formed. Upfield shifts of the aromatic protons are indicative of cytosine deprotonation and metal binding to N^4.[3,14] Readjustment of the pD of the solution to 5 (NaOH) and/or addition of an excess of $[Pd(en)(D_2O)_2]^{2+}$ leads to an increase in intensity of the product signals. These findings are to be interpreted in terms of any of the following possibilities. (*i*) Formation of a trinuclear $PtPd_2$ species with head-to-tail arranged cytosinato ligands and mixed N^4,O^2 co-ordination spheres for both Pd^{II}(en) entities; (*ii*) formation of a dinuclear complex with a single Pd^{II}(en) bound to two N^4 nitrogen atoms; (*iii*) formation of a trinuclear complex with the two Pd^{II}(en) entities co-ordinated pairwise to two N^4 and two O^2 oxygen atoms, respectively. Elemental analysis of the isolated compound ruled out (*ii*), but only X-ray crystallography could differentiate between (*i*) and (*iii*) and eventually proved the compound to be of type (*i*).

Table 1 Co-ordination bond distances (Å) and angles (°) for $[Pt(NH_3)_2(mcyt)_2\{Pd(en)_2\}][NO_3]_4$. Primed atoms at $-x, y, \frac{1}{2}-z$

Pt···Pd	2.9365(6)	Pd–O(2)	2.034(6)
Pt–N(2)	2.039(6)	Pd–N(4)	2.030(7)
Pt–N(3)	2.037(6)	Pd–N(5)	2.022(7)
		Pd–N(6)	2.013(8)
Pd···Pt···Pd′	166.79(2)	O(2)–Pd–N(4)	93.1(3)
N(2)–Pt–N(2′)	90.1(3)	O(2)–Pd–N(5)	89.2(3)
N(2)–Pt–N(3)	90.0(2)	O(2)–Pd–N(6)	171.8(3)
N(2)–Pt–N(3′)	179.2(3)	N(4)–Pd–N(5)	172.1(3)
N(3)–Pt–N(3′)	89.9(2)	N(4)–Pd–N(6)	93.0(3)
		N(5)–Pd–N(6)	84.0(3)

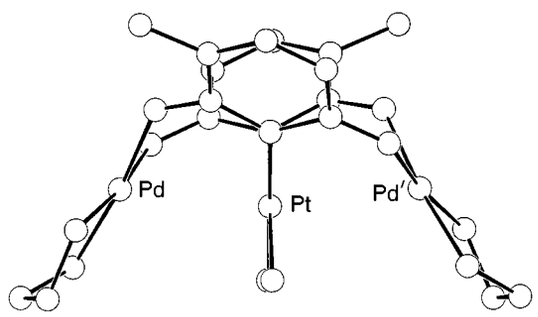


Fig. 2 A side view of the trinuclear cation along the N(3)–N(3′) direction, giving the impression of a 'molecular insect'

A perspective view of the trinuclear cation is given in Fig. 1. The d^8 metal ions present the usual square-planar co-ordination and the Pt is positioned on a crystallographic two-fold axis, bisecting the N^3–Pt–$N^{3'}$ angle. The nucleobases act as trifunctional ligands towards the metals through the endocyclic N^3 to Pt, the oxygen O^2 and the deprotonated amino group N^4 to Pd. Their mean planes form a dihedral angle of 96.5(1)°. The resulting arrangement for the nucleobases is head-to-tail and the co-ordination Pt–N^3, Pd–N^4, Pd–O^2 distances are 2.037(6), 2.030(7) and 2.034(6) Å, respectively. The other co-ordination sites of Pt and both Pd are occupied by NH_3 and ethane-1,2-diamine, respectively. A selection of bond lengths and angles is reported in Table 1. The co-ordination mean planes of each Pd and of Pt make an angle of 32.8(2)°, so that the dihedral angle between the two Pd co-ordination planes is 65.6 °. The Pd···Pt···Pd′ angle is 166.79(2)°, as evidenced from Fig. 2, where the cation is viewed along the N^3–$N^{3'}$ direction.

The Pt···Pd distance of 2.9365(6) Å is slightly, but significantly, longer than the values of 2.837(1) and 2.839(1) Å found in the trinuclear species *cis*-$[\{Pt(NH_3)_2(mura\text{-}N^3,O^4)_2\}_2Pd]^{2+}$,[16] but it is very close to the value of 2.927(1) Å, found in the dinuclear *cis*-$[(NH_3)_2Pt(mura\text{-}N^3,O^4)_2Pd(en)]^{2+}$ species (mura = 1-methyluracilate).[17]

In the crystal the distances between adjacent cations, *e.g.* PdPtPd···PdPtPd, are 5.834(1) Å, and no significant hydrogen bonding is detected between the complexes and the nitrate anions.

Reactions with *trans*-$[Pd(NH_3)_2(D_2O)_2]^{2+}$ and *cis*-$[Pt(NH_3)_2(D_2O)_2]^{2+}$

Reaction of *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$ with an excess of *trans*-$[Pd(NH_3)_2(D_2O)_2]^{2+}$ produces several new cytosine ^{1}H NMR resonances upfield from the original sets, indicative of cytosine deprotonation and Pd^{II} co-ordination to N^4. The most intense

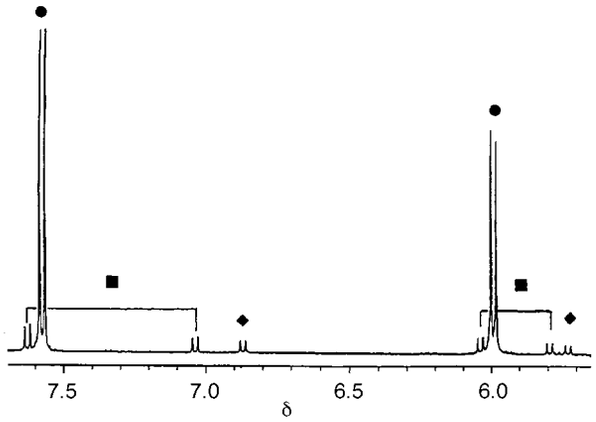


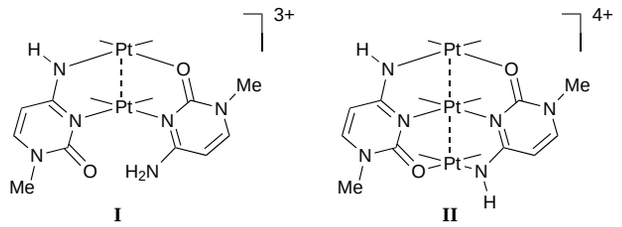
Fig. 3 Section of ^{1}H NMR spectrum (400 MHz, D_2O, sodium 3,3,3-trimethylpropanesulfonate) of *cis*-$[Pt(NH_3)_2(Hmcyt)_2][NO_3]_2$ with *cis*-$[Pt(NH_3)_2(D_2O)_2][NO_3]_2$ (40 h, 35 °C, pD 3.7 after initial adjustment to 5.6). Resonances are assigned to Hmcyt of the starting compound (●), to mcyt of the Pt_3 compound (◆), and to Hmcyt/mcyt of the Pt_2 compound (■)

new mcyt resonances are close to resonances observed for the trinuclear $PtPd_2$ compound (*cis*-$[Pt(NH_3)_2(mcyt)_2\{Pd(en)\}_2][NO_3]_4$), suggesting a similar composition. Considering the established lability of the NH_3 ligands of *trans*-$Pd^{II}(NH_3)_2$ and its propensity for isomerization,[18] a rearrangement of *trans*-$Pd^{II}(NH_3)_2$ to the corresponding *cis* species and binding to N^4 and O^2 seems likely.

With *cis*-$[Pt(NH_3)_2(D_2O)_2]^{2+}$ added to *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$ (pD kept at *ca.* 5 by addition of NaOD) three sets of new cytosine resonances of low intensity appear with time (Fig. 3), two of which are upfield from the respective H^5 and H^6 cytosine doublets of the starting compound. Two of these upfield shifted doublets (δ 6.87 and 5.72) are very close to those of the $PtPd_2$ compound and are therefore assigned to the corresponding Pt_3 complex. The two other sets, one upfield and one downfield of the original resonances and of equal intensities, are consistent with a species containing two non-equivalent cytosine ligands, a neutral and an anionic one. A Pt_2 complex of composition *cis*-$[Pt(NH_3)_2(Hmcyt)(mcyt)Pt(NH_3)_2]^{3+}$, with the second Pt entity binding to the deprotonated N^4 position of the mcyt ligand and to O^2 of Hmcyt, would perfectly account for these resonances. Thus Pt_2 (**I**) could be the expected intermediate between the mononuclear starting compound and Pt_3 (**II**).

If reaction between *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$ and *cis*-$[Pt(NH_3)_2(D_2O)_2]^{2+}$ (0.05 mM each) is carried out without NaOD added, resonances assigned to the Pt_3 species represent 10–15% of those of the starting compound within 4 d at 40 °C. At this point the original H^6 doublet of Pt_3 has simplified to a singlet due to isotopic H→D exchange at the 5 position.[19] During the initial phase of the reaction (≈1 d, 40 °C), the pD of the solution drops from *ca.* 5.1 to *ca.* 2.2, presumably as a consequence of deprotonation of the exocyclic amino group of Hmcyt and binding of $Pt(NH_3)_2$. Apparently, in a parallel reaction, a species is formed which gives rise to a broad and poorly structured set of resonances at δ 7–7.4. Its intensity slowly increases over several weeks (sample at 22 °C), gaining an intensity of *ca.* 15–20% of the original H^6 doublet of *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$. The appearance of these new resonances is accompanied by formation of an initially light blue and at a later stage of a dark black-blue colour. A typical UV/VIS spectrum, recorded after 4 weeks at 22 °C (NMR sample), displays rather broad bands at around 530 and 680 nm. Absorption coefficients of these absorptions, based on *cis*-$[Pt(NH_3)_2(Hmcyt)_2]^{2+}$ and taking into consideration a 20% turnover, are in the order of $\varepsilon \approx 10^5$ cm^{-1} M^{-1}, qualifying them as charge transfer bands.

It was also noted that, following the initial sharp drop in pD,

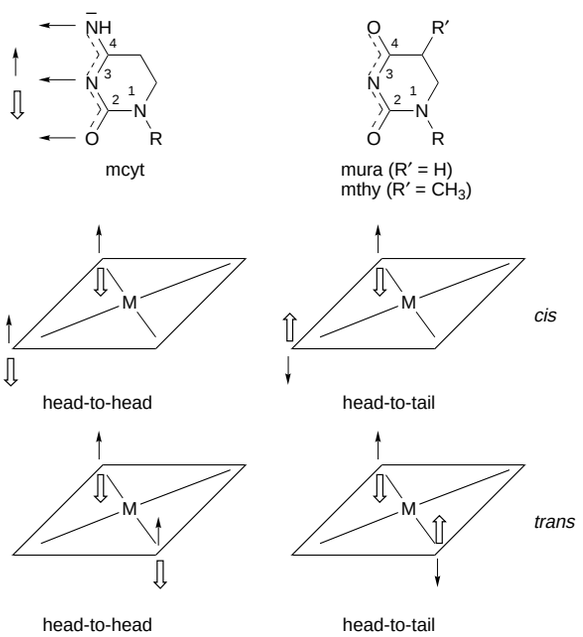


there was later a gradual rise again in pD, from 2.2 to 3.9 (within 4 weeks). Since there was no decrease in signal intensity of the mcyt resonances (H^6 and N–CH_3) assigned to Pt_3, reprotonation of N^4 and displacement of Pt from this site, has to be excluded as an explanation. Liberation of NH_3 from either two starting compounds may explain this observation. Taken together, both the broad resonances in the ^{1}H NMR spectrum and the intense colour suggest formation of a 'platinum blue'.[20] This conclusion is supported by the fact that aged solutions display the typical EPR features of 'platinum pyrimidine blues' (with $g_\perp \approx 2.42$ and $g_\parallel \approx 2.04$, D_2O, frozen solution), although in the present case the signals are considerably weaker than in previously published ones.[21]

Conclusion

We consider the compound, *cis*-$[Pt(NH_3)_2(mcyt)_2\{Pd(en)_2\}][NO_3]_4$, described in this work an important piece in the puzzle provided by multinuclear complexes of N^1-blocked pyrimidine nucleobases, notably of Hmcyt, but also of the related nucleobases 1-methyluracil (Hmura) and 1-methylthymine (Hmthy). These three nucleobases, in their anionic forms, have in common the propensity of forming di- and oligo-nuclear metal complexes once the N^3 position is carrying a Pt^{II} or Pd^{II} entity. Most likely this feature is not restricted to these metal ions. As we have demonstrated in many instances,[22] formation of di- or multi-nuclear species is particularly pronounced in the case of the respective bis(nucleobase) complexes, *e.g.* with *cis*- or *trans*-$M^{II}am_2L_2$ (am = NH_3 or amine; M = Pt or Pd; L = nucleobase or its anion) or with *trans*-PtI_2L_2. Ignoring mixed-nucleobase complexes, which we have studied to a limited extent,[23] four principal types of trinuclear complexes can be derived from square-planar MX_2L_2 (Scheme 1), depending on the geometry of M (*cis* or *trans*) and the mutual orientation of the two nucleobases (head-to-head or head-to-tail). As far as stoichiometries are concerned, the following conclusions can be drawn. First, M,M′,L_2 stoichiometries (M′ = second metal, bonded through exocyclic groups of L) are very common for head-to-head arranged bases L, irrespective of *cis*- or *trans*-geometry of M. Atom M′ binds to two O^4 sites of deprotonated Hmura or Hmthy[15,16] or two N^4 sites of mcyt.[14] Subsequent binding of a third metal ion (M″) is possible to give M,M′,M″,L_2. It takes place at the O^2 sites[3,24] and generally requires an excess of M″, which suggests that basicities of O^4,O^4 and N^4,N^4 combinations are substantially higher than those of O^2,O^2. Secondly, despite a very limited number of crystallographically characterized examples with head-to-tail ML_2 complexes the stoichiometry of the established cases is M,M′$_2$,L_2.[25–27] This is also true for the $PtPd_2$ complex described here. This finding tentatively suggests that combining a good and a poor donor site, *viz.* N^4 and O^2 of mcyt, and O^4 and O^2 of mura or mthy, is particularly advantageous for the formation of trinuclear complexes containing a central ML_2 entity.

We are planning to study further trinuclear $PtPd_2$ and in particular Pt_3 complexes with regard to their redox chemistry. Partially oxidized species would be ideally suited to form oligomeric stacks, thereby possibly producing yet another type of 'platinum blue' which consists of trinuclear building blocks rather than dinuclear ones as previously seen,[28,29] or truely polymeric ones, as proposed.[30]



Scheme 1 Trinuclear complexes derived from square-planar MX_2L_2 compounds

Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft (DFG), the Fonds der Chemischen Industrie (FCI), Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome) and Consiglio Nazionale delle Ricerche (CNR, Rome). We thank Mr. Jacobi and Professor Lehnig for recording the EPR spectrum.

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Received 24*th June* 1997; *Paper* 7/04460G