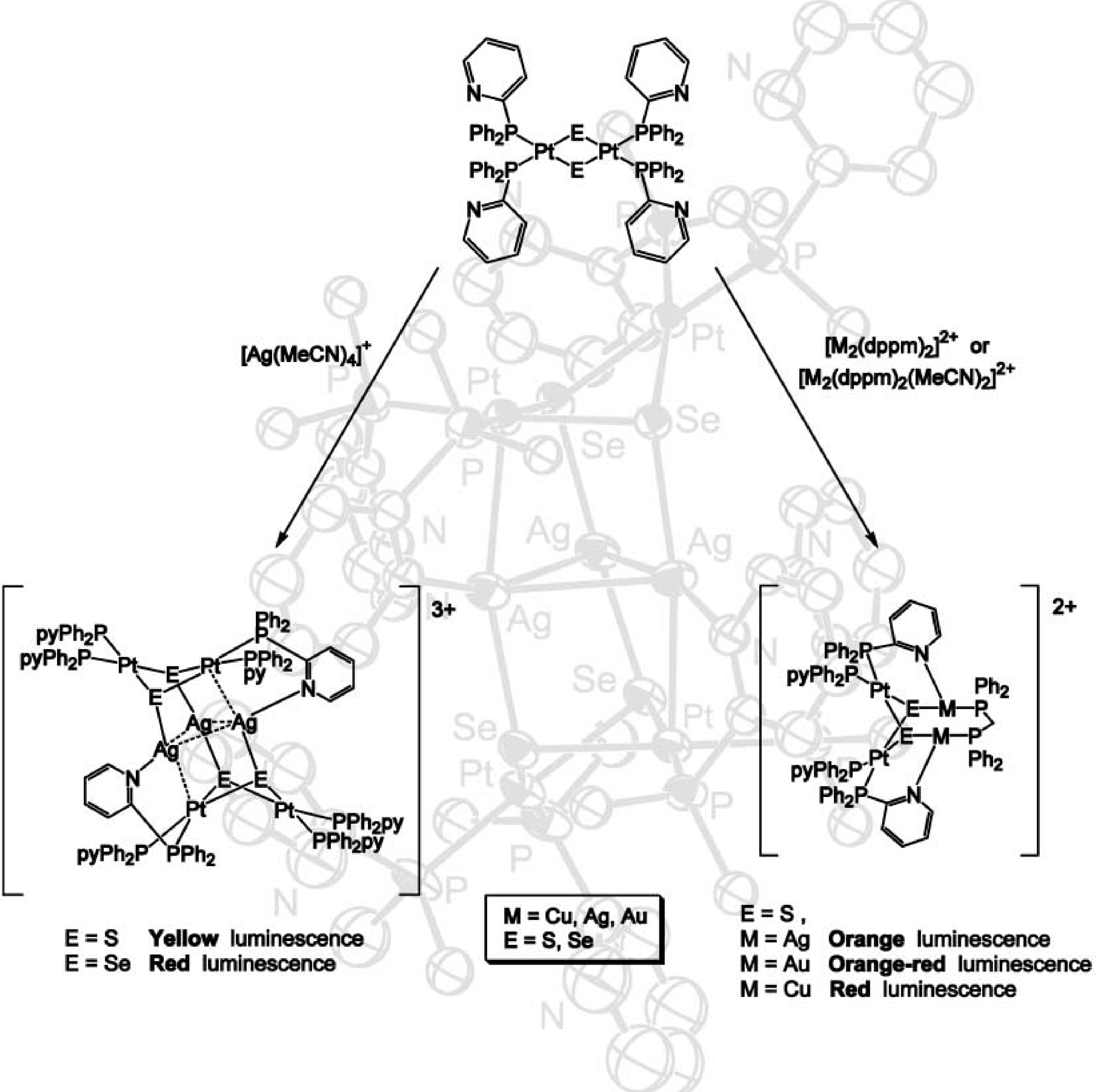
Luminescent Homo- and Heteropolynuclear Platinum(II) Chalcogenido Aggregates



E = S **Yellow** luminescence
E = Se **Red** luminescence

M = Cu, Ag, Au
E = S, Se

E = S ,
M = Ag **Orange** luminescence
M = Au **Orange-red** luminescence
M = Cu **Red** luminescence

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Luminescent Homo- and Heteropolynuclear Platinum(II) Chalcogenido Aggregates Based on $[Pt_2E_2(P\hat{}N)_4]$ Units (E = S, Se)

Vivian Wing-Wah Yam,* Ka-Lai Yu, Eddie Chung-Chin Cheng, Phyllis Kok-Yan Yeung, Kung-Kai Cheung, and Nianyong Zhu[a]

Abstract: A series of homodinuclear platinum(II) complexes containing bridging chalcogenido ligands, $[Pt_2(\mu\text{-}E)_2(P\hat{}N)_4]$ (P^N = dppy, E = S (**1**), Se (**2**); P^N = *t*Bu-dppy, E = S (**3**)) (dppy = 2-(diphenylphosphino)pyridine, *t*Bu-dppy = 4-*tert*-butyl-2-(diphenylphosphino)pyridine) have been synthesized and characterized. The nucleophilicity of the $\{Pt_2E_2\}$ unit towards a number of d^{10} metal ions and complexes has been demonstrated through the successful isolation of a number of novel heteropolynuclear platinum(II)–copper(I), –silver(I), and –gold(I) complexes: $[\{Pt_2(\mu_3\text{-}E)_2(dppy)_4\}_2Ag_3](PF_6)_3$ (E = S (**4**); Se (**5**)) and $[Pt_2(dppy)_4(\mu_3\text{-}E)_2M_2(dppm)]X_2$ (E = S, M = Ag, X = BF_4 (**6**); E = S, M = Cu, X = PF_6 (**7**); E = S, M = Au, X = PF_6 (**8**); E = Se, M = Ag, X = PF_6 (**9**); E = Se, M = Au, X = PF_6 (**10**)). Some of them display short metal⋯metal contacts. These complexes have been found to possess interesting luminescence properties. Through systematic comparison studies, the emission origin has been probed.

Keywords: chalcogens · luminescence · platinum · selenium · sulfur

Introduction

Metal–chalcogen coordination chemistry has attracted much attention because of its significance in semiconductors, catalysis, and biological science. These compounds may serve as model systems in providing a better understanding on the underlying mechanism and development of new techniques in these fields. Many molecular transition-metal chalcogenido complexes also function as precursors for the synthesis of inorganic solid-state compounds under relatively moderate conditions.[1] Among such derivatives, part of the attention has been drawn to the d^8 metal complexes that have a variable number of chalcogen and metal atoms in their inner core and which possess certain interesting properties.[2–4] The simplest type consists of two chalcogen and two metal atoms (M_2S_2). In 1970, Chatt and Mingos first reported the synthesis of the diplatinum(II) complex, $[Pt_2(\mu\text{-}S)_2(PMe_2Ph)_4]$ that had a hinged square-planar geometry.[5] A similar complex, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ was reported by Ugo et al. in 1971.[6]

The nucleophilic and donor properties of $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ towards various d-block transition-metal ions and complexes were established in the early 1980s.[7–9] These studies were further extended to the p-block metals, which has recently been reviewed by Hor and co-workers.[10] Recently, we synthesized a related complex, $[Pt_2(\mu\text{-}S)_2(dppy)_4]$ (**1**, dppy = 2-diphenylphosphinopyridine), which serves as a metalloligand; both the complex and its heterometallic aggregates are luminescent and have been subjected to photophysical investigations.[11, 12] It is believed that the employment of dppy instead of the conventionally used PR_3 would provide extra coordination sites that might serve to stabilize complexes of higher nuclearity. Despite growing interest in the use of the Pt_2S_2 core as a metalloligand, relatively little attention has been directed to the heavier Pt_2Se_2 congener, which should exhibit better nucleophilic behavior.[13, 14] The luminescence properties of this class of complexes are also relatively unexplored. As a continuation of our efforts in the field of transition metal chalcogenides,[15–19] we report here on two newly synthesized metalloligands, $[Pt_2(\mu\text{-}E)_2(P\hat{}N)_4]$ (P^N = dppy, E = Se **2**; P^N = *t*Bu-dppy, E = S **3**) and their heterometallic aggregates (Scheme 1). The heteropolynuclear aggregates formed by the nucleophilic coordination of $[Pt_2(\mu\text{-}E)_2(dppy)_4]$ (E = S, Se) to silver(I) and $[M_2(dppm)]$ (M = Cu, Ag, Au) units are also described. The photophysical properties of the newly synthesized complexes are also reported.

Results and Discussion

Synthesis and characterization: The new dinuclear platinum(II) chalcogenido complexes **2** and **3** were prepared by a modification of the previously reported synthetic procedure

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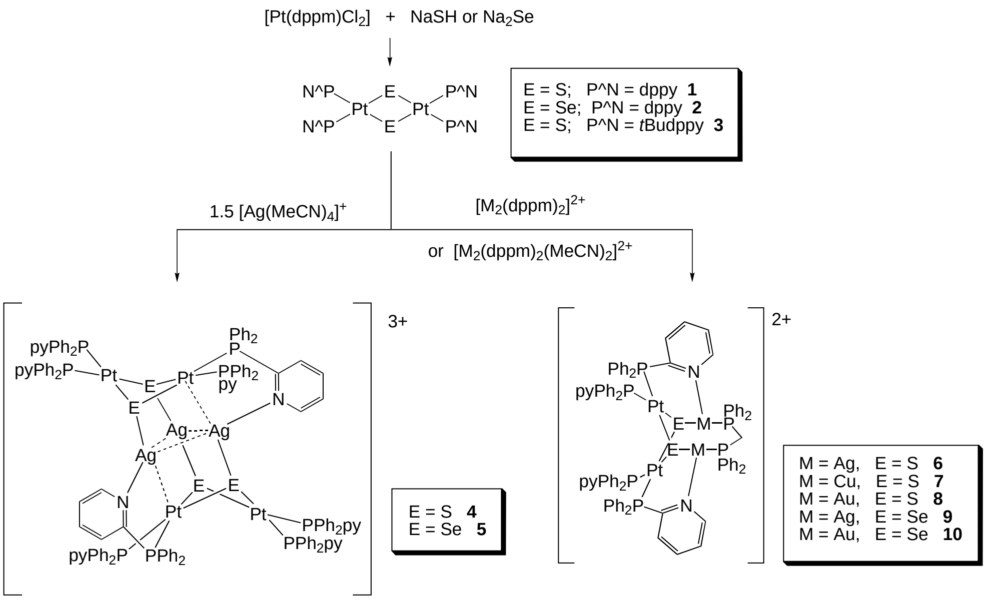

Scheme 1.

for **1**, in which the reaction of $[Pt(dppy)_2Cl_2]$ and $[Pt(tBu\text{-}dppy)_2Cl_2]$ with sodium chalcogenide in acetonitrile gave the respective desired products. Any unreacted sodium chalcogenide was readily removed by filtration. The choice of solvents for the purification of **2** and **3** were limited because of the reactivity of the complexes with halogenated solvents, similar to the analogous complex **1**. Ligands **1** and **2** were found to have poor solubility in common organic solvents, whereas **3**, with the introduction of a *tert*-butyl group at the pyridyl ring of the dppy ligands, has good solubility in most common organic solvents.

It is well documented that, in the presence of lone pairs on the bridging sulfur atoms, $[Pt_2(\mu\text{-}S)_2(PPh_3)_4]$ is capable of coordinating to other metal centers to thus function as a metalloligand for the synthesis of heterometallic aggregates. Upon replacement of a phenyl group in PPh_3 by a 2-pyridyl group, namely with a dppy ligand, it is believed that the presence of an extra coordination site would further stabilize the electrophilic metal centers. In the previous communication, the reaction of **1** with the electrophilic silver(I) center gave a highly novel heptanuclear heterometallic platinum(II)–silver(I) complex, $[\{Pt_2(\mu_3\text{-}S)_2(dppy)_4\}_2Ag_3](PF_6)_3$ (**4**), which was structurally characterized. It exhibits rich photophysical and photochemical properties.[11] As a continuation of our recent interests in the chemistry of heterometallic aggregates, a similar reaction with $[Pt_2(dppy)_4(\mu\text{-}Se)_2]$ gave the analogous heterometallic selenido platinum(II)–silver(I) aggregate, $[\{Pt_2(\mu_3\text{-}Se)_2(dppy)_4\}_2Ag_3](PF_6)_3$ (**5**), which has also been structurally characterized.

The perspective drawing of the complex cation of **5** is shown in Figure 1. Table 1 summarizes the

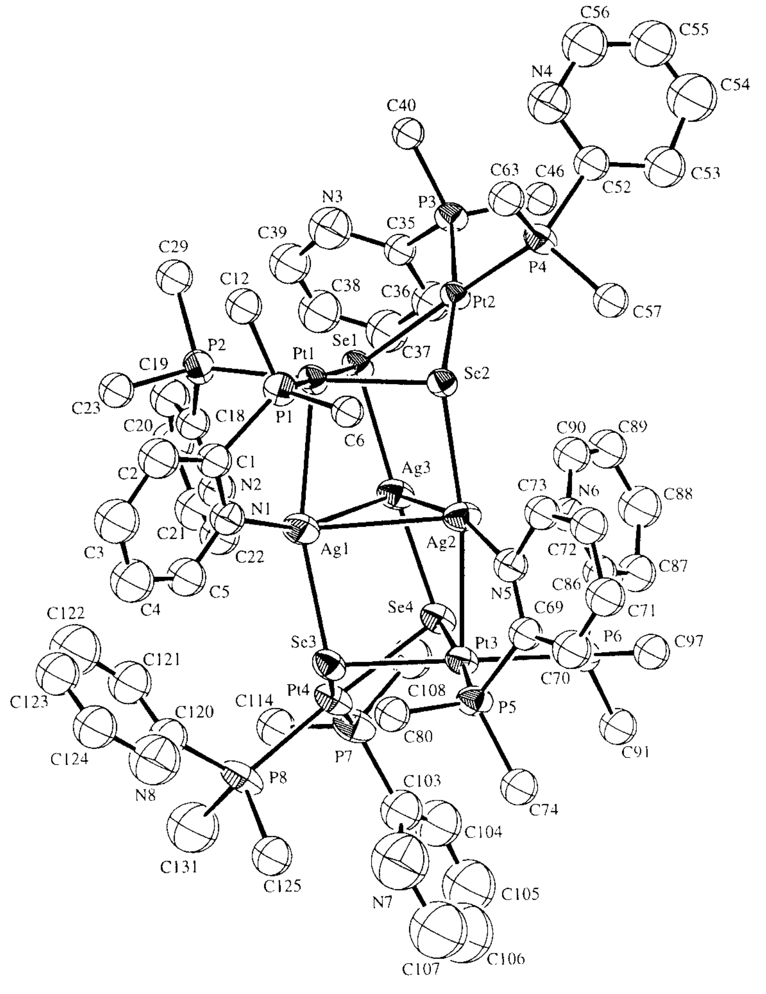

Figure 1. Perspective drawing of the complex cation of $[\{Pt_2(dppy)_4(\mu_3\text{-}Se)_2\}_2Ag_3](PF_6)_3$ (**5**) with the atomic numbering scheme. Only the *ipso*-carbon atoms of the phenyl rings on the phosphorus atoms are shown for clarity. Thermal ellipsoids are shown at the 30% probability levels.

Table 1. Selected bond lengths [Å] and bond angles [°] for **5**.

Pt1−Ag1	2.8277(9)	Pt3−Ag2	2.7838(9)
Pt1−Se1	2.477(1)	Pt2−Se1	2.460(1)
Pt1−Se2	2.4622(9)	Pt2−Se2	2.4732(9)
Pt3−Se3	2.459(1)	Pt4−Se3	2.481(1)
Pt3−Se4	2.467(1)	Pt4−Se4	2.459(1)
Ag3−Se1	2.508(1)	Ag3−Se4	2.505(1)
Ag1−Se3	2.593(1)	Ag2−Se2	2.594(1)
Ag1−N1	2.410(9)	Ag2−N5	2.404(9)
Ag1−Ag2	3.014(1)	Ag2−Ag3	2.852(1)
Ag1−Ag3	2.882(1)	Pt2−P3	2.292(2)
Pt1−P1	2.284(3)	Pt3−P6	2.298(3)
Pt1−P2	2.308(3)	Pt4−P7	2.294(3)
Pt3−P5	2.292(3)		
Ag1-Pt1-Se1	91.57(3)	Ag1-Pt1-Se2	94.68(3)
Ag2-Pt3-Se3	91.42(3)	Ag2-Pt3-Se4	83.21(4)
Ag1-Pt1-P1	90.50(8)	Ag1-Pt1-P2	88.91(8)
Ag2-Pt3-P5	93.84(8)	Ag2-Pt3-P5	93.84(8)
Ag2-Pt3-P6	90.71(8)	Se1-Pt1-P1	175.31(7)
Se1-Pt1-Se2	83.32(3)	Se2-Pt1-P1	92.32(7)
Se1-Pt1-P2	85.77(7)	P1-Pt1-P2	98.48(10)
Se2-Pt1-P2	168.60(7)	Se3-Pt3-P5	92.40(8)
Se3-Pt3-Se4	83.21(4)	Se4-Pt3-P5	175.59(8)
Se3-Pt3-P6	169.67(8)	P5-Pt3-P6	97.5(1)
Se4-Pt3-P6	86.83(8)	Se1-Pt2-P3	90.15(7)
Se1-Pt2-Se2	83.43(3)	Se2-Pt2-P3	172.31(7)
Se1-Pt2-P4	170.65(7)	P3-Pt2-P4	98.38(9)
Se2-Pt2-P4	87.77(7)	Se3-Pt4-P7	171.65(8)
Se3-Pt4-Se4	82.91(4)	Se4-Pt4-P7	89.20(8)
Se3-Pt4-P8	86.36(9)	P7-Pt4-P8	101.2(1)
Se4-Pt4-P8	168.02(8)	Ag1-Ag2-Ag3	58.78(3)
Ag2-Ag1-Ag3	57.79(3)	Ag1-Ag3-Se1	89.65(4)
Ag1-Ag3-Ag2	63.43(3)	Ag2-Ag3-Se1	101.30(4)
Ag1-Ag3-Se4	97.36(4)	Se1-Ag3-Se4	172.40(5)
Ag2-Ag3-Se4	84.56(4)	Pt1-Ag1-Ag3	79.02(3)
Pt1-Ag1-Ag2	80.31(3)	Pt1-Ag1-N1	82.5(2)
Pt1-Ag1-Se3	164.10(4)	Ag2-Ag1-N1	117.2(2)
Ag2-Ag1-Se3	83.85(4)	Ag3-Ag1-N1	161.4(2)
Ag3-Ag1-Se3	91.44(4)	Pt3-Ag2-Ag1	83.52(3)
Se3-Ag1-N1	106.2(2)	Pt3-Ag2-Se2	170.80(4)
Pt3-Ag2-Ag3	84.55(3)	Ag1-Ag2-Se2	87.73(3)
Pt3-Ag2-N5	82.1(2)	Ag3-Ag2-Se2	88.48(3)
Ag1-Ag2-N5	115.9(2)	Ag3-Ag2-N5	166.2(2)
Pt1-Se1-Pt2	85.06(3)	Pt1-Se1-Ag3	93.56(4)
Pt2-Se1-Ag3	109.96(4)	Pt1-Se2-Pt2	85.08(3)
Pt1-Se2-Ag2	96.38(4)	Pt2-Se2-Ag2	118.46(4)
Ag1-N1-C1	128.8(7)	Ag2-N5-C69	130.4(7)
Se2-Ag2-N5	104.4(2)		

selected bond lengths and angles; the crystallographic data can be found in the Experimental Section. The structure of the complex cation of **5** consists of an Ag_3 unit sandwiched between two $[Pt_2(\mu_3\text{-}Se)_2(dppy)_4]$ units to give an overall barrel-shaped structure, isostructural to that of the related sulfido analogue **4**. The Pt ⋯ Pt distances of 3.3369 – 3.3696 Å and Ag – Ag distances of 2.852 – 3.014 Å are suggestive of the presence of weak metal ⋯ metal interactions. The Pt1−Ag1 and Pt3−Ag2 bond lengths of 2.8277(9) and 2.7838(9) Å, respectively, are also suggestive of weak Pt ⋯ Ag interactions.[20] The Pt−Se and Ag−Se bond lengths have values of 2.459(1) – 2.481(1) and 2.505(1) – 2.594(1) Å, respectively, which are slightly longer than the metal – chalcogen bond lengths observed in **4** (Pt−S: 2.339 – 2.359 Å; Ag−S: 2.430 – 2.489 Å), as one would have expected.[11] The $[Pt_2(dppy)_4(\mu_3\text{-}Se)_2]$ metalloligand moiety in **5** has a hinged square-planar geometry, with a dihedral angle of 129 – 130°. The Ag-Ag-Ag angles are in the range of 57.79(3) – 63.43(3)°, which are not far from that of 60° for an equilateral triangle observed in a related Ag_3 cluster.[21] The Se1-Ag3-Se4 angle of 172.40(5)° is close to linearity. The Se2-Ag2-Pt3 and Se3-Ag1-Pt1 angles of 170.80(4) and 164.10(4)°, and Se3-Ag1-N1 and Se2-Ag2-N5 angles of 106.2(2) and 104.4(2)° are distorted from those of a perfect T-shaped geometry, probably as a result of the steric demand required for the barrel-shaped structure.

In addition to the electrophilic silver(I), dinuclear metal complexes with bridging diphosphine ligands can also be employed in the synthesis of new heterometallic aggregates. Indeed, **1** and **2** have been shown to be able to act as a metalloligand to coordinate to the {M_2dppm} units (M = Cu, Ag, Au), forming complexes **6** – **10**. Figure 2 also shows the proposed structure of **6** – **10**, with the two platinated chalcogen atoms coordinated to the {M_2dppm} unit in a bridging fashion. Each d^{10} metal center is further stabilized by a pyridyl nitrogen atom.

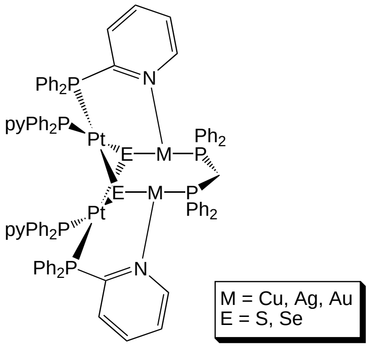

Figure 2. Proposed structure of complexes **6** – **10**.

Electronic absorption and emission studies: All the complexes are found to exhibit interesting luminescence properties, and the electronic absorption and emission data are summarized in Table 2. The electronic absorption spectra of the platinum(II) chalcogenido complexes **1** – **3** have low-energy absorption bands or shoulders at $\lambda = 425 - 488$ nm with extinction coefficients in the order of 10^3 $dm^3 mol^{-1} cm^{-1}$. The low-energy absorptions, which were not present in $[Pt(dppy)_2Cl_2]$, $[Pt(\textit{t}Bu\text{-}dppy)_2Cl_2]$, dppy and *t*Bu-dppy, are likely to be characteristic of the platinum(II) chalcogenido core. Therefore, it is suggested that the origin of these low-energy transitions should not be derived from the dppy intraligand (IL) nor the metal-to-ligand charge transfer (MLCT) $[d(Pt) \rightarrow \pi^*(dppy)]$ transitions. By comparison of the electronic absorption spectra data of **1** and **2**, it is likely that the low-energy absorption, which shows a red shift from **1** to **2**, may arise from a ligand-to-metal charge transfer (LMCT) $[E^{2-} \rightarrow Pt]$ (E = S or Se) transition, in agreement with the good σ-donating capability of the chalcogenido moiety. However, an assignment of a ligand-to-ligand charge transfer (LLCT) $[E^{2-} \rightarrow dppy]$ transition could also give rise to the observed trend.

Similarly, the low-energy absorptions at $\lambda > 350$ nm in the heterometallic aggregates **4** – **10** are unlikely to be derived from an IL [dppy] or MLCT $[d(Pt) \rightarrow \pi^*(dppy)]$ transition.

Table 2. Photophysical data for the platinum(II) chalcogenido complexes.

	Absorption in MeCN at 298 K λ_{max} [nm] (ε_{max} [dm^3 mol^{-1} cm^{-1}])	Emission Medium (T [K])	λ_{em} [nm] (τ_0 [μs])
[Pt$_2$(dppy)$_4$(μ-S)$_2$] (**1**)[a]	350 (8000), 425sh (3000)	solid (298)	645 (10.0 ± 0.5)
		solid (77)	635
[Pt$_2$(dppy)$_4$(μ-Se)$_2$] (**2**)	300 (20580), 440 (970)[c]	solid (298)	695 (2.1 ± 0.2)
		solid (77)	680
[Pt$_2$(tBu-dppy)$_4$(μ-S)$_2$] (**3**)	282 (111360), 488 (7570)	solid (298)	640 (4.0 ± 0.4)
		solid (77)	630
		glass (77)[d]	610
		MeCN (298)	540
[{Pt$_2$(dppy)$_4$(μ_3-S)$_2$}$_2$Ag$_3$](PF$_6$)$_3$ (**4**)[b]	262sh (51000), 394sh (2900)	solid (298)	560 (< 0.1)
		solid (77)	560, 635sh
		glass (77)[d]	560, 630sh
		MeCN (298)	600 (<0.1)
[{Pt$_2$(dppy)$_4$(μ_3-Se)$_2$}$_2$Ag$_3$](PF$_6$)$_3$ (**5**)	294sh (85200), 350sh (15590), 428sh (4300)	solid (77)	735
		glass (77)[d]	665
		MeCN (298)	655
[Pt$_2$(dppy)$_4$(μ_3-S)$_2$Ag$_2$(dppm)](BF$_4$)$_2$ (**6**)[b]	262sh (47900), 394sh (1225)	solid (298)	630 (1.5 ± 0.2)
		solid (77)	660
		glass (77)[d]	630 (51.0 ± 0.5)
[Pt$_2$(dppy)$_4$(μ_3-S)$_2$Cu$_2$(dppm)](PF$_6$)$_2$ (**7**)	262sh (48,090), 402sh (960)	solid (77)	695
		glass (77)[d]	710 (31.0 ± 0.5)
		MeCN (298)	650
[Pt$_2$(dppy)$_4$(μ_3-S)$_2$Au$_2$(dppm)](PF$_6$)$_2$ (**8**)	262sh (47800), 352sh (3,505)	glass (77)[d]	660 (30.0 ± 0.5)
		MeCN (298)	570
[Pt$_2$(dppy)$_4$(μ_3-Se)$_2$Ag$_2$(dppm)](PF$_6$)$_2$ (**9**)	258sh (79830), 350sh (8200), 430sh (1340)	solid (77)	635
		glass (77)[d]	650
[Pt$_2$(dppy)$_4$(μ_3-Se)$_2$Au$_2$(dppm)](PF$_6$)$_2$ (**10**)	262sh (65270), 350sh (1930)	solid (77)	670
		glass (77)[d]	645

[a] From Ref. [12]. [b] From Ref. [11]. [c] In THF. [d] EtOH-MeOH, 4:1 v/v.

However, a definite assignment of the low-energy absorption shoulders is not possible, since the electronic absorption spectra are fairly featureless.

Complexes **1**–**3** show intense orange emission in the solid state, both at room temperature and at 77 K, upon photoexcitation at $\lambda > 350$ nm. The solid-state emission spectra of **1** and **2** at 77 K are shown in Figure 3. The long excited-state lifetime observed at room temperature suggests that the emission is most likely to be associated with a spin-forbidden triplet-state transition. Metal-perturbed IL transition is unlikely to be responsible for the emission of **1**–**3**, as free dppy and the tBu-dppy ligand are found to emit at ≈480 nm in the solid state, that is, much higher in energy than the complexes. Moreover, in view of the large Pt–Pt separation (3.555(1) Å) as revealed in the structure of **1**,[11] an emissive state derived from a [$d_\sigma^* \rightarrow p_\sigma$] transition that results from a d_{z^2}–d_{z^2} and a p_z–p_z orbital overlap in d^8–d^8 metal–metal bonded systems (where d_σ^* is the antibonding combination of d_{z^2}–d_{z^2} overlap and p_σ is the bonding combination of the p_z–p_z overlap taking the Pt–Pt axis as the z axis)[22] is also unlikely. Neither is this low-energy emission band appeared to be derived from a MLCT [d(Pt) → π*(dppy)] origin because of its absence in the [Pt(dppy)$_2$Cl$_2$] counterpart. A further comparison between **1** and **2** suggests that the low-energy emitting state should arise from states bearing a large amount of LMCT [p(E^{2-}) → d(Pt)] (E = S or Se) character, in agreement with the better σ-donating capability of the selenido than the sulfido moiety. On the other hand, comparison of **1** and **3** shows that there is not much difference in the emission energy between the two, although a close scrutiny revealed that **3** emits at slightly higher energy than **1**. This is suggestive of some involvement of the dppy and tBu-dppy ligand in the transition. Thus, the emission is likely to consist of a large proportion of LMCT character, with some involvement of a LLCT character.

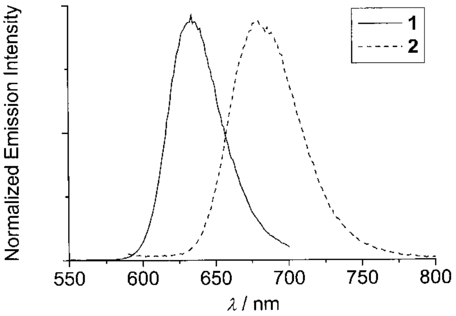

Figure 3. Solid-state emission spectra of complexes **1** and **2** at 77 K.

For the heptanuclear heterometallic aggregates **4** and **5**, low-energy emissions were observed in the solid state, in 77 K glass, and in solution. A red shift in emission energies has been observed upon going from **4** to **5** in the 77 K solid state, 77 K EtOH/MeOH glass, and room temperature MeCN emission spectra. This is suggestive of an assignment of the HOMO (highest-occupied molecular orbital) as predominantly chalcogenide in character. The contribution of the metal-centered (MC) [d-s/d-p] states is also possible, based on the observation of weak metal ··· metal interactions (Pt ··· Ag and Ag ··· Ag) in their crystal structures. An assignment of an emitting state bearing a large chalcogenide-to-metal LMCT character, or alternatively, a metalloligand-to-metal charge transfer

[$Pt_2E_2 \rightarrow Ag_3$] character that mixed with MC [d-s/d-p] states is suggested.

In the tetranuclear $M_2E_2M'_2$ series **6**–**10**, a systematic spectroscopic comparison of the structural variation of M′ and E would provide insights into the origin of the emissive states. In the series **6**–**8**, the emission energies in 77 K glass are in the order **7** < **8** ≤ **6** (Figure 4). The red shift in the emission energy of **7** relative to **6** may be suggestive of an emitting state bearing a large LMCT character. Copper(I) sulfido or dithiolate clusters are known to have a lower energy emission than their silver(I) counterparts.[23–26] Likewise, the emission observed in **6** and **7** is dominated by states derived from a LMCT [$E^{2-} \rightarrow$ Cu/Ag] transition mixed with a LMCT [$E^{2-} \rightarrow$ Pt] state of the platinum chalcogenido core. An alternative assignment that is derived from states of a [$Pt_2(\mu\text{-}E)_2(dppy)_4 \rightarrow M$] metalloligand-to-metal charge transfer transition is also possible. This has been further supported by the observation of a red shift in emission energy of **9** in 77 K glass relative to that of **6**. However, a blue shift in the 77 K solid-state emission of **9** relative to **6** is found. It is likely that the origin of the emission is derived from states bearing an admixture of LMCT and MC character.[23–25]

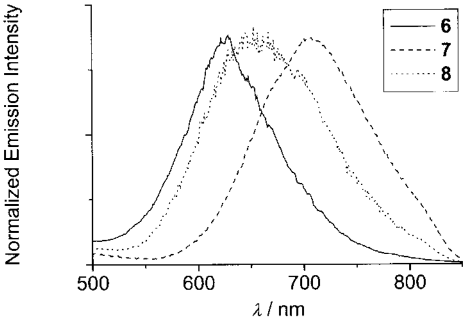

Figure 4. Emission spectra of complexes **6**, **7** and **8** at 77 K EtOH/MeOH (4:1 v/v) glass.

The anomalous emission energy trends of **8** ≤ **6**, **10** ≈ **9** and **8** ≤ **10** in 77 K EtOH/MeOH glass are suggestive of an emission origin that could not have been derived from a pure LMCT emissive state. It is likely that short Au⋯Au distances may exist in **8** and **10**, as is commonly found in polynuclear gold(I) systems.[27–30] It is also likely that the emissive states of **8** and **10** are derived from a mixed LMCT/d-p character, whereby the d-p character becomes more prominent in the gold(I) system as a result of the stronger metal–metal bonding interaction of gold relative to copper and silver.[26] An alternative assignment as a ligand-to-metal–metal-bond charge transfer (LMMCT) or a metalloligand-to-metal–metal-bond charge transfer origin is also likely. Similar assignments have also been suggested in the dinuclear Au^I thiolate systems[31–37] and the polynuclear gold(I) sulfido systems,[17–19] in which the emission origin was assigned as the respective [$RS^- \rightarrow Au$] and [$S^{2-} \rightarrow Au$] LMCT states, modified by weak Au⋯Au interactions, or alternatively, the LMMCT states.

Experimental Section

Materials and reagents: The ligand bis(diphenylphosphino)methane (dppm) and [$Pt(cod)Cl_2$] were purchased from Strem Chemicals. 2-(Diphenylphosphino)pyridine (dppy),[38, 39] NaSH,[40] Na_2Se,[41] [$Ag(MeCN)_4$]PF_6,[42] [$Cu_2(dppm)_2(MeCN)_2$]$(PF_6)_2$,[43] [$Ag_2(dppm)_2(MeCN)_2$]$(PF_6)_2$,[44] [$Au_2(dppm)_2$]$(PF_6)_2$,[45] and [$Pt(dppy)_2Cl_2$][46] were synthesized according to published procedures. 4-*tert*-Butyl-2-(diphenylphosphino)pyridine and [$Pt(t\text{Bu-dppy})_2Cl_2$] were prepared by modification of a method published for dppy and [$Pt(dppy)_2Cl_2$], respectively. The synthesis and characterization of complexes **1**, **4**, and **6** have been reported in previous communications.[11, 12] All solvents were purified and distilled in a nitrogen atmosphere by means of standard procedures prior to use. All other reagents were of analytical grade and were used as received.

Physical measurements and instrumentation: ^1H NMR spectra were recorded on a Bruker DPX300 (300 MHz) FT-NMR spectrometer, with chemical shifts (δ) reported relative to Me_4Si. Elemental analyses of all the newly synthesized metal complexes were performed either at the Butterworth Laboratories or on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, the Chinese Academy of Sciences in Beijing. All positive-ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. All electronic absorption spectra were recorded on a Hewlett–Packard 8452A diode array spectrophotometer.

Steady-state emission and excitation spectra recorded at room temperature and at 77 K were obtained on a Spex Fluorolog-2 Model F111 fluorescence spectrophotometer with or without corning filters. All solutions for photophysical studies were prepared in a two-compartment cell consisting of a 10 cm^3 Pyrex bulb equipped with a side-arm and attached to a quartz cuvette (path length: 1 cm), and sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were degassed under high vacuum (limiting pressure $< 10^{-3}$ torr) with no less than four successive freeze-pump-thaw cycles. Solid-state photophysical measurements were carried out with solid samples loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the Dewar flask for low-temperature (77 K) solid-state and glass photophysical measurements.

Emission lifetime measurements were performed with a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150–10 pulsed Nd-YAG laser. Luminescence decay signals were recorded on a Tektronix model TDS620A digital oscilloscope, and analyzed with a program for exponential fits.

Synthesis: All reactions were carried out with standard Schlenk techniques under an inert atmosphere of nitrogen.

[$Pt_2(dppy)_4(\mu\text{-}Se)_2$] (2): Na_2Se (47 mg, 0.379 mmol) was added to a suspension of [$Pt(dppy)_2Cl_2$] (100 mg, 0.126 mmol) in MeCN (10 mL). The reaction mixture turned yellow and an orange precipitate formed immediately. The reaction mixture was stirred for an additional 24 h at room temperature. The resulting solid was filtered and washed successively with 95% EtOH, absolute EtOH, Me_2CO, and Et_2O. Analytically pure samples of **2** were obtained by recrystallization from benzene. Yield: 25 mg (25%); positive FAB-MS: m/z: 1602 [M^+]; elemental analysis calcd (%) for $C_{68}H_{56}N_4P_4Pt_2Se_2 \cdot 1.5\,H_2O$ (1628.2): C 50.19, H 3.65, N 3.44; found: C 50.15; H 3.48, N 3.25.

[$Pt_2(t\text{Bu-dppy})_4(\mu\text{-}S)_2$] (3): NaSH (19 mg, 0.332 mmol) and NEt_3 (46 μL, 0.332 mmol) were added to a suspension of [$Pt(t\text{Bu-dppy})_2Cl_2$] (100 mg, 0.111 mmol) in MeCN (10 mL). The reaction mixture turned orange instantly. After stirring at room temperature for 24 h, the resulting solution was filtered and concentrated under reduced pressure. Addition of petroleum ether (b.p. 40–60 °C) to the red solution afforded **3** as an air-stable orange precipitate. Yield: 29 mg (30%); ^1H NMR (CD_3CN): δ = 0.95–1.35 (m, 36H; *t*Bu), 7.10–8.30 (m, 52H; phenyl); positive FAB-MS: m/z: 1730 [M^+]; elemental analysis calcd (%) for $C_{84}H_{88}N_4P_4Pt_2S_2 \cdot 4.5\,H_2O$ (1812.9): C 55.65, H 5.04, N 3.11; found: C 55.66, H 5.36, N 3.09.

[$\{Pt_2(dppy)_4(\mu_3\text{-}Se)_2\}_2Ag_3$]$(PF_6)_3$ (5): [$Ag(MeCN)_4$]PF_6 (20 mg, 0.047 mmol) in MeCN (10 mL) was added dropwise to a suspension of **2** (50 mg, 0.031 mmol) in THF (10 mL). The suspension immediately turned into a clear yellow solution. Stirring was continued for 1 h under N_2. The resulting solution was reduced in volume and subsequent precipitation by addition of diethyl ether into its concentrated solution gave a yellow solid, which was then recrystallized from MeCN/Et_2O to give **5** as air-stable yellow crystals. Yield: 37 mg (30%); ^{1}H NMR (CD$_3$CN): $\delta = 6.85-7.95$ (m, phenyl); positive FAB-MS: m/z: 1176 [$M^{3+} - 3\,PF_6$]; elemental analysis calcd (%) for $C_{136}H_{112}Ag_3F_{18}N_8P_{11}Pt_4Se_4$ (3960.8): C 41.24, H 2.85, N 2.83; found: C, 41.28, H 2.74, N 2.69.

[Pt$_2$(dppy)$_4$(μ_3-S)$_2$Cu$_2$(dppm)](PF$_6$)$_2$ (7): [Cu$_2$(dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$ (41 mg, 0.033 mmol) in MeCN (10 mL) was added dropwise to a suspension of **1** (50 mg, 0.033 mmol) in THF (10 mL). The suspension immediately turned into a clear yellow solution. Stirring was continued for 1 h under N$_2$. The resulting solution was reduced in volume and subsequent precipitation by addition of diethyl ether into its concentrated solution gave a yellow solid. Recrystallization from MeCN/Et$_2$O gave **7** as air-stable yellow crystals. Yield: 43 mg (60%); ^{1}H NMR (CD$_3$CN): $\delta = 3.6$ (m, 2H; CH$_2$ of dppm), 7.0–8.0 (m, 72H; phenyl of dppm), 8.18 (d, 4H; H *ortho* to N of py); positive FAB-MS: m/z: 2163 [$M^+ - PF_6$], 2018 [$M^+ - 2\,PF_6$], 1009 [$M^{2+} - 2\,PF_6$]; elemental analysis calcd (%) for $C_{93}H_{78}Cu_2F_{12}N_4P_8Pt_2S_2 \cdot 0.5\,MeCN$ (2329.3): C 48.5, H 3.4, N 2.7; found: C 48.9, H 3.3, N 2.5.

[Pt$_2$(dppy)$_4$(μ_3-S)$_2$Au$_2$(dppm)](PF$_6$)$_2$ (8): The procedure used was similar to that described for the preparation of complex **7** except that [Au$_2$(dppm)$_2$](PF$_6$)$_2$ (48 mg, 0.033 mmol) was used in place of [Cu$_2$(dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$. Recrystallization from MeCN/Et$_2$O gave **8** as air-stable yellow crystals. Yield: 51 mg (60%); ^{1}H NMR (CD$_3$CN): $\delta = 4.0$ (m, 2H; CH$_2$ of dppm), 7.0–8.0 (m, 72H; phenyl of dppm), 8.4 (d, 4H; H *ortho* to N of py); positive FAB-MS: m/z: 2431 [$M^+ - PF_6$], 2284 [$M^+ - 2\,PF_6$], 1142 [$M^{2+} - 2\,PF_6$]; elemental analysis calcd (%) for $C_{93}H_{78}Au_2F_{12}N_4P_8Pt_2S_2$ (2575.6): C 43.4, H 3.1, N 2.2; found: C 43.5, H 3.0, N 2.1.

[Pt$_2$(dppy)$_4$(μ_3-Se)$_2$Ag$_2$(dppm)](PF$_6$)$_2$ (9): The procedure used was similar to that described for the preparation of complex **7** except that **2** (50 mg, 0.031 mmol) and [Ag$_2$(dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$ (42 mg, 0.031 mmol) were used in place of **1** and [Cu$_2$(dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$, respectively. Recrystallization from MeCN/Et$_2$O gave **9** as air-stable yellow crystals. Yield: 19 mg (25%); ^{1}H NMR (CD$_3$CN): $\delta = 3.65$ (m, 2H; CH$_2$ of dppm), 6.85–8.00 (m, 72H; phenyl), 8.20 (d, 4H; H *ortho* to N of py); positive FAB-MS: m/z: 1101 [$M^{2+} - 2\,PF_6$]; elemental analysis calcd (%) for $C_{93}H_{78}Ag_2F_{12}N_4P_8Pt_2Se_2$ (2491.2): C 44.84, H 3.16, N 2.25; found: C 44.89, H 2.99, N 2.10.

[Pt$_2$(dppy)$_4$(μ_3-Se)$_2$Au$_2$(dppm)](PF$_6$)$_2$ (10): The procedure used was similar to that described for the preparation of complex **7** except that **2** (50 mg, 0.031 mmol) and [Au$_2$(dppm)$_2$](PF$_6$)$_2$ (45 mg, 0.031 mmol) were used instead of **1** and [Cu$_2$(dppm)$_2$(MeCN)$_2$](PF$_6$)$_2$, respectively. Recrystallization from MeCN/diethyl ether gave **10** as air-stable yellow crystals. Yield: 25 mg (30%); ^{1}H NMR (CD$_3$CN): $\delta = 3.75$ (m, 2H; CH$_2$ of dppm), 6.90–7.85 (m, 72H; phenyl), 8.20 (d, 4H; H *ortho* to N of py); positive FAB-MS: m/z: 2380 [$M^+ - 2\,PF_6$], 1190 [$M^{2+} - 2\,PF_6$]; elemental analysis calcd (%) for $C_{93}H_{78}Au_2F_{12}N_4P_8Pt_2Se_2 \cdot 2\,H_2O$ (2705.5): C 41.29, H 3.05, N 2.07; found: C 41.12, H 2.86, N 1.77.

Crystal structure determination: Brown crystals of **5** were obtained by recrystallization from MeCN/Et$_2$O. A brown crystal of dimensions $0.35 \times 0.20 \times 0.15$ mm mounted on a glass fiber was used for data collection at 28 °C on a MAR diffractometer that employed graphite-monochromatic Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and which was equipped with a 300 mm image plate detector. The images were interpreted and intensities integrated with the program *DENZO*.[47] The space group was determined on the basis of a statistical analysis of the intensity distribution and the successful refinement of the structure solved by direct methods (*SIR 92*[48]) and expanded by Fourier method and refinement by full-matrix least-squares with the software package *TeXsan*[49] on a Silicon Graphics Indy computer. One crystallographic asymmetric unit consisted of one asymmetric unit, that is, the complex cation, 3PF$_6^-$, and 5MeCN solvent molecules. In the least-square refinement, 22 Pt, Ag, Se, and P atoms were refined anisotropically, 177 F, N, and C atoms were refined isotropically and 100 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. 12 H atoms of the complex cation and 15 H of the solvent molecules were not included in the calculations. Data: formula: $C_{136}H_{112}N_8P_8Se_4Ag_3Pt_4 \cdot 3\,PF_6 \cdot 5\,CH_3CN$; $M_r = 4164.17$; crystal system: triclinic, space group: $P\bar{1}$, $a = 19.437(3)$, $b = 19.828(3)$, $c = 22.161(3)$ Å, $\alpha = 73.90(2)$, $\beta = 84.35(2)$, $\gamma = 71.43(2)^\circ$, $V = 7778(2)$ Å^3, $Z = 2$; $F(000) = 4016$, $\rho_{calcd} = 1.778$ g cm^{-3}, $\mu = 50.6$ cm^{-1}; $2\theta_{max} = 51.3^\circ$; index range: $0 \leq h \leq 23$, $-22 \leq k \leq 24$, $-26 \leq l \leq 26$. Data collection mode 2° oscillation (100 images), 120 mm distance, 700 s exposure; no. of data collected = 80413, no. of unique data = 27042 (R_{int} 0.054), no. of data used in refinement (m) = 20277 ($F_o > 3\sigma(F_o)$), no. of parameters refined (p) = 909; $R(F_o) = 0.053$, $wR(F_o) = 0.079$, $S = 2.11$ with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.024\,F_o^2)^2]$; $S = [\Sigma w(|F_o| - |F_c|)^2/(m-p)]^{1/2}$. $(\Delta/\sigma)_{max} = 0.05$, except for atoms of the solvent molecules. The final difference Fourier map was featureless, with maximum positive and negative peaks of 1.42 and 1.73 e Å^{-3} respectively. CCDC-187036 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

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