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Platinum Stacking Interactions in Homoleptic Platinum Polymers

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Recent breakthroughs in low-dimensional nanostructures have led to a renewal of interest in polymers composed of platinum complexes. The surge of research into one-dimensional platinum complexes in the 1970s and 1980s has given way to a steady progression of investigations that have explored new ligands, characterization techniques and applications. The ongoing synthesis and characterization of new tetra(cyano)platinate, bis(oxalato)platinate and other homoleptic platinum complexes has allowed examination of the influence of organic and inorganic cations on the Pt–Pt distance and the importance of small molecules in stabilizing the stacking interactions. In particular, complexes of $[\mathrm{Pt}(\mathrm{C{\equiv}NR})_4]^{2+}$ and $[\mathrm{Pt^I(bipy)_2}]^+$ show potential to display short stacking interactions. This microreview focuses on the progress in the synthesis and characterization of homoleptic complexes with short Pt–Pt distances and avenues for the development of new classes of complexes.

Introduction

It is remarkable to consider that although platinum-based complexes that display one-dimensional polymer formation were synthesized well over 150 years ago, their unique properties were not recognized until the middle of the twentieth century. Bis(oxalato)platinate (BOP) complexes have been known since the work of Dobereiner in 1835,[1] but the ability of these complexes to form one-dimensional metal-linked polymers was not fully recognized until the work of Krogmann in the late 1960s.[2] More recently, however, the unique properties of low dimensionality materials have been recognized and utilized immediately. After the observation of carbon nanotubes by Iijima in 1991, these unique organic materials found application in many diverse areas within a few years.[3,4] Recent progress in the synthesis of zero-dimensional quantum dots,[5,6] one-dimensional metal oxides,[7,8] and two-dimensional “nano-

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mesh"[9] suggests that unique properties and novel applications of new low-dimensional inorganic materials will continue to be discovered and developed. One-dimensional polymers of iridium are well known and research into these complexes is ongoing.[10,11] One-dimensional structures of rhodium,[12] palladium,[13] and cobalt[14] are also the subjects of considerable research interest.

A key feature contributing to the novel properties of platinum complexes is the ability for direct Pt–Pt atom overlap of the predominately d_{z^2} orbitals. It has been known for some time that in solution and the solid state, this net interaction between adjacent square-planar platinum complexes leads to the formation of a columnar-stacked chain structure.[15–17] In the 1960s Krogmann demonstrated that partial oxidation of the platinum complexes could lead to polymeric structures with Pt–Pt distances almost as short as the bonds in platinum metal (ca. 2.77 Å).[18–21]

Computational modelling along with the ongoing synthesis and characterization of novel stacked platinum complexes has given new insights into the factors influencing the interaction between adjacent complexes.[22–25] The technological potential for platinum complexes with short Pt–Pt bonds has been realized through the development of materials that act as sensors for the detection of volatile organic compounds.[26–30] There are a great number of *heteroleptic* platinum complexes with short Pt–Pt bond lengths and there has been substantial work on the characterization and spectroscopic properties of these platinum complexes by Gray, Eisenberg, Schanze and others.[27,31–34] These systems provide a useful examination of the effect of combinations of different ligand types. Many sulfur-containing platinum complexes such as $[Pt(mnt)_2]^{2-}$ (mnt = *cis*-1,2-dicyano-1,2-ethylenedithiolate) have been observed to form columnar structures; however, in these examples bonding also occurs from overlap of molecular orbitals of the sulfur, phosphorus or other atoms on the ligands.[35] These systems have recently been reviewed in detail by Kato,[36] and are not the focus of this review.

The intention of this review is to summarize progress made in homoleptic platinum complexes with significant Pt–Pt overlap (≤ 3.5 Å) where the platinum metal overlap is the primary bonding interaction. The Abbott group has long been interested in platinum chemistry where understanding and predicting the structure of square-planar platinum complexes has been a prime objective.[37–41] Over the last twenty years, significant progress has been made by many groups in understanding the factors that control the interaction between platinum complexes; this review will also highlight areas of research where additional advances may yet be made.

Complexes with Pt–C Bonds

The strength of Pt–C bonds is due in part to the ability of the complex to engage in significant π-back-bonding interactions.[22] Although the existence of one of the simplest complexes; tetramethylplatinum(IV), has been disputed,[42,43] numerous other platinum complexes with Pt–C bound ligands have been reported (see Figure 1).

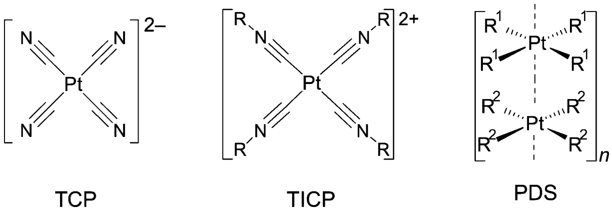

Figure 1. Structure of tetra(cyano)platinate(II) (TCP), tetra(isocyanide)platinum(II) (TICP) and platinum double salt (PDS) complexes.

Cyanide Ligands

Knop and Schnedermann originally reported that the oxidation of $K_2[Pt(CN)_4]\cdot 3H_2O$ with bromine gave copper-coloured needles upon evaporation.[44,45] The later work of Krogmann demonstrated these crystals to be polymers with the formula $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, and Krogmann and co-workers demonstrated that partial oxidation could be brought about by a range of cations and anions.[46–49] Miller first codified the factors that favour the formation of one-dimensional polymers.[50,51] These criteria include: 1) Use of third-row d^8 complexes to maximize the $5d_{z^2}$ orbital; 2) Use of transition metals with smaller nuclear charge to prevent contraction of the $5d_{z^2}$ orbital; 3) Use of a negatively charged complex to prevent contraction of the $5d_{z^2}$ orbital; 4) Use of small non-bulky ligands to prevent steric repulsion between adjacent complexes; 5) Use of strong field ligands to enhance d–π* back bonding; and 6) hydrogen bonding between individual complexes to stabilize the one-dimensional system. Given these criteria the affinity of platinum complexes, specifically tetra(cyano)platinate(II) (TCP) complexes, to form one-dimensional systems is not unexpected. What is not incorporated in Miller's criteria is the effect of cations and other small molecules, including solvent molecules. These small molecules are critical to stabilizing the stacked structure, and loss of water molecules in the case of $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ leads to rapid loss of structure and conductivity. The divalent complex $K_2[Pt(CN)_4]\cdot 3H_2O$ has been well characterized with a Pt–Pt distance of 3.478(1) Å, but more recently Jansen and co-workers have determined the crystal structures of anhydrous $K_2[Pt(CN)_4]$ and the analogous monohydrated complex $K_2[Pt(CN)_4]\cdot H_2O$ (see Table 1).[52] Surprisingly the Pt–Pt distance changes only slightly between the two complexes, despite water molecules in the monohydrated structure linking additional adjacent TCP units together. In the analogous tetra(cyano)palladate(II) complexes, the Pd–Pd bond length is notably longer in both the anhydrous [4.3303(2) Å] and hydrated [3.607(1) Å] complexes.

Jansen and co-workers also recently reported the synthesis of hydrogen peroxide adducts of alkali metal tetra(cyano)platinates $A_2[Pt(CN)_4]\cdot H_2O_2$ (A = K, Rb, Cs).[53,54] This is an unexpected result due to the tendency for hydro-

Table 1. Platinum–platinum bond lengths in tetra(cyano)platinate(II) complexes.

Complex	Pt···Pt distance [Å]	Ref.
$K_2[Pt(CN)_4]$	3.520(2)	[52]
$K_2[Pt(CN)_4]\cdot H_2O$	3.579(1)	[52]
$K_2[Pt(CN)_4]\cdot H_2O_2$	3.2730	[53]
$Rb_2[Pt(CN)_4]\cdot H_2O_2$	3.2841	[53]
$Cs_2[Pt(CN)_4]\cdot H_2O_2$	3.2928	[53]
$Rb_2[Pt(CN)_4]$	3.719(0)	[57]
$Rb_2Ba[Pt(CN)_4]_2$	3.389(3) 3.582(3)	[58]
$Er_2[Pt(CN)_4]_3\cdot 21H_2O$ (Red form)	3.1891(3) 3.1625(5)	[59]
$Er_2[Pt(CN)_4]_2\cdot SO_4\cdot 11.5H_2O$ (Yellow form)	3.2687(9) 3.4003(9)	[59]
[1,1′-dimethyl-4,4′-bipyridinium]$[Pt(CN)_4]$	7.748	[60]
$[N\text{-}(n\mathrm{Bu})_4]_2[Pt(CN)_4]$	9.542	[60]
[4,4′-bipiperidinium]$[Pt(CN)_4]\cdot H_2O$	7.980	[61]
[Ru(1,10-phenanthroline)$_2$(2,2′bipyridine)]-$[Pt(CN)_4]$	13.134	[62]
[Cu(2,2′bipyridine)$_2$]$[Pt(CN)_4]$	7.767	[63]
$[Cu(en)_2][Pt(CN)_4]$	6.560	[64]
[Pt(2-aminopyridine)(2,2′bipyridine)]-$[Pt(CN)_4]\cdot 2H_2O$	4.560, 5.203, 7.297	[65]

gen peroxide to convert the divalent tetracyanoplatinates to the known partially oxidized analogues.[55] The tetra(cyano)platinate units all rotated relative to adjacent units by approximately 45° as observed in other TCP complexes.[56] The new series of complexes have Pt–Pt distances in the range of 3.27 to 3.52 Å, with the H_2O_2 molecules engaged in hydrogen bonding to the cyano ligands. The critical factor in the growth of the crystals is to use a solution pH close to 7, preventing the formation of the partially oxidized complexes.[54]

Muhle et al. were able to synthesize the anhydrous mixed cation complex $Rb_2Ba[Pt(CN)_4]$ which possesses two distinct Pt–Pt distances of 3.389(3) Å and 3.582(3) Å. These differing Pt–Pt distances correspond to the alternating rubidium and barium ions, respectively. In the unit cell, the cations form primitive cubic polyhedra with eight nitrogen atoms on adjacent cyanide ligands bound to either the rubidium [Rb–N distance: 3.33(1) Å] or barium cations [Ba–N distance = 2.90(2) Å]. The presence of the divalent barium cation is also of interest because few examples of TCP complexes containing divalent cations have been isolated.[66,67] TCP complexes that possess mixed monovalent and divalent cations including $K_2Sr[Pt(CN)_4]_2\cdot 2H_2O$ and $K_2Sr[Pt(CN)_4]_2\cdot 6H_2O$ have been reported previously with short Pt–Pt distances.[49] Nevertheless, none of these new complexes exhibit Pt–Pt distances as short as those in the analogous partially oxidized TCP systems. Tetracyanoplatinate polymers incorporating metal cations from the lanthanide and actinide series have given important insight into energy transfer between the platinum chain and the metal cation. Examples of tetracyanoplatinate chains with all of the trivalent lanthanide counterions have been characterized with the exception of Pm^{3+} due to its rarity and short half-life.[68] Loosli et al. have recently crystallized the red and yellow forms of erbium tetracyanoplatinate that correspond to $Er_2[Pt(CN)_4]_3\cdot 21H_2O$ and $Er_2[Pt(CN)_4]_2\cdot SO_4\cdot 11.5H_2O$ respectively.[59] These two complexes display two different Pt–Pt distances due to the ratio of cation to anion packing. Despite the increase in the numbers of waters of hydration from 11.5 to 21 the red $Er_2[Pt(CN)_4]_3\cdot 21H_2O$ complex shows shorter Pt–Pt distances [3.1891(3) Å] than the yellow $Er_2[Pt(CN)_4]_2\cdot SO_4\cdot 11.5H_2O$ complex [3.2687(9) Å] due to incorporation of a single sulfate molecule into the unit cell of the latter. Replacement of metal cations with organic cations in TCP systems does not lead to retention of short Pt–Pt distances.[69] Despite the planar nature of the methyl viologen cation (1,1′-dimethyl-4,4′-bipyridinium), this and other organic cations lead to structures with Pt–Pt distances >5 Å.[60] Despite the lack of close Pt–Pt interactions, this complex exhibits intense, polarized luminescence at 545 nm due to a charge transfer interaction between the cations and anions. Maynard and Skyora have characterized the related complex [4,4′-bipiperidinium]$[Pt(CN)_4]\cdot H_2O$ which adopts a similar structure with no short Pt–Pt interactions due to the alternating cation-anion pairs.[61] Although the luminescent properties were not studied in this complex, the lack of a π-delocalized system in the 4,4′-bipiperidinium cation is likely to prevent charge-transfer interactions. Several examples of TCP compounds with sulfur-containing organic conductors such as tetrathiafulvalene have been studied.[70–72] Single-crystal studies of this family of complexes demonstrate that the TCP units do not have any direct Pt–Pt overlap and conduction occurs purely through the organic cations.[73–76]

The inability to incorporate diverse ligands severely restricts the potential for molecular diversity in TCP systems. Replacement of small inorganic cations with coordinated metal complexes also disrupts the packing of the TCP stacking interaction. Tetrahedral cations such as [Cu(2,2′bipyridine)$_2$]$^{2+}$ and $[Cu(en)_2]^{2+}$ lead to Pt–Pt distance >5 Å.[63,64] The incorporation of the bulky octahedral ligand [Ru(1,10-phenanthroline)$_2$(2,2′bipyridine)]$^{2+}$ also prevents close approach of the TCP units. The X-ray crystal structure of [Pt(2-aminopyridine)(2,2′-bipyridine)][Pt$(CN)_4]\cdot 2H_2O$ has been reported with an alternating cation-anion structure.[65] The Pt–Pt separation is 4.560 Å and 5.203 Å between the platinum atoms of the anion and cation and 7.297 Å between individual TCP centres. The interaction of the 2-amino group on the cation prevents closer approach of the cation-anion units, suggesting that short Pt–Pt distances may be possible with appropriate ligand substitution. Hydrogen bonding of water molecules and hydrogen ions within the complex may also play a role in stabilizing the overall structure.

In addition to the synthesis of new complexes, new instrumental techniques have allowed for a detailed examination of the underlying physical properties of TCP systems. Scanning tunnelling microscopy (STM) has been used to observe the structure of $K_{1.75}[Pt(CN)_4]\cdot 1.5H_2O$ and the stacked TCP units are clearly visible.[77] Atomic force microscopy (AFM) observations confirmed the columnar structure of electrochemically oxidized $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$ with a Pt–Pt spacing of 2.89 Å, comparable with the dimensions determined by single-crystal X-ray diffraction.[78] These studies indicate that growth occurs primarily along the crystallographic *c*-axis, corresponding to the terminal TCP unit via a layer spreading mechanism. The AFM probe tip allowed for deformation of the surface of the TCP crystal and an examination of freshly exposed surface to a depth of several nanometers.[79] Importantly AFM measurements allowed for the observation of the hydration-dehydration of TCP single crystals. Upon slow dehydration of the crystal, the average Pt–Pt distance lengthens by approximately 30% with notable disordering along the Pt–Pt axis. Recovery was observed almost immediately upon rehumidification of the dry crystal. Several authors have suggested the technological potential of TCP complexes to act as vapochromic or humidity sensors.[80,81]

Platinum(II) complexes with cyanide ligands have historically received significant attention due to their straightforward synthesis, relative stability, and novel conduction and luminescent properties. Nevertheless, engineering of these properties is impeded by the inability to systematically modify these complexes. Introduction of metal cations has allowed for structure-property relationships to be elucidated, but introduction of structurally diverse organic ligands disrupts the critical Pt–Pt interaction. In addition, the loss of waters of crystallization leads to a disordering of the crystalline structure and loss of the unique material properties.

Isocyanide Ligands

The criteria suggested by Miller favour the formation of TCP-based polymers, but the formation of polymers of homoleptic tetra(isocyanide)platinum (TICP) complexes is not observed despite the similarities in electronic structure between the TCP and TICP systems.[82] Greater steric interaction between the ligands, the electropositive charge on the TICP complexes and the weaker π-acceptor character of the isocyanide ligand all serve to decrease the tendency for these platinum complexes to form columnar structures. A search of the Cambridge Structural Database (CSD) produced only 17 structures of general formula $[Pt(CNR)_4]^{2+}$ with the majority being heteroleptic “platinum double salts” (PDS) of formula $[Pt(CNR)_4][PtCl_4]$.[83–86] Single crystal X-ray analyses of $[M(CNCH_3)_4][PF_6]_2$ (M = Pt and Pd) reveal the unit cells to be isostructural with individual square planar units arranged perpendicular to one another with metal–metal distances >5 Å (see Figure 2). The Pt–Pt bond lengths in platinum isocyanide complexes can be highly variable as evidenced in *cis*-$[Pt(4\text{-}CNC_6H_4\text{-}C_2H_5)_2(CN)_2]$ where the average Pt–Pt distance is 3.2905(2) Å, compared to *cis*-$[Pt(CNC_2H_5)_2(CN)_2]$ where the Pt–Pt distance is at least 5 Å.[87,88]

The lack of structurally characterized, homoleptic TICP complexes prevents more detailed comparisons. The small number of homoleptic TICP complexes found in the literature was unexpected given the structural diversity that substituted isocyanide ligands could introduce. Although the positively charged complex may cause contraction of the $5d_{z^2}$ orbitals, this remains an area of significant potential. Although PDS complexes are outside the scope of this review the observation that crystals of $[Pt(CNC_6H_5)_4][PtCl_4]$ are blue-violet in colour is suggestive of interaction between the $5d_{z^2}$ orbitals with short Pt–Pt distances, and a reinvestigation of this salt and its homoleptic analogue $[Pt(CNC_6H_5)_4]^{2+}$ may be warranted.[89,90]

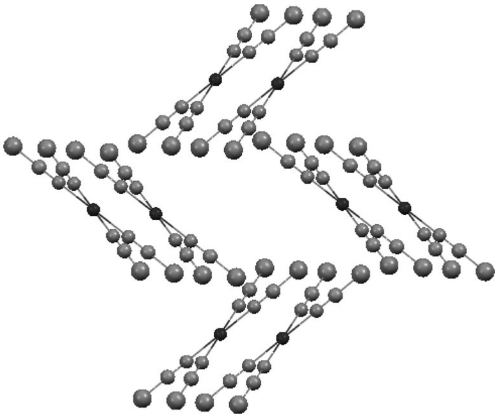

Figure 2. ORTEP plot of $[Pt(CNCH_3)_4][PF_6]_2$ at 30% probability level generated from the data deposited with the CSD. Anions not shown.

Acetylide Ligands

Homoleptic acetylide complexes of the general formula $K_2[Pt(C{\equiv}CR)_4]$ (R = H, Me, Ph) were first reported by Nast and Heinz.[91] No information is given regarding the Pt–Pt distances, but the description of $K_2[Pt(C{\equiv}CPh)_4]$ as an ochre solid suggests a UV/Vis absorption that may be attributed to short Pt–Pt interactions. The instability of these complexes prompted Moreno and co-workers to synthesize a similar series of complexes with bulky substituents to prevent nucleophilic attack.[92] These substituted platinum acetylides were stable in air, but the use of bulky substituents disrupted the platinum stacking interactions. More recently, Zhang et al. have synthesized a bidentate acetylide ligand that forms a strained square planar structure upon coordination to platinum.[93] In this case, the enforced planarity of the arene rings assists in minimizing steric interactions, however the use of the $[NBu_4]^+$ cation prevents close Pt–Pt packing due to steric interactions.

Forniés and co-workers have produced a series of platinum acetylide complexes in which the stacking interactions are modulated by the presence of small metal ions such as Cd^{2+}, Ag^+ and Tl^+.[94–96] The crystal structure of $[Pt_2Ag_4(C{\equiv}CC_6H_4\text{-}3\text{-}OMe)_8]_\infty$ is typical of this class of complexes (see Figure 3). The two Pt–Pt distances are 3.1458(8) Å and 4.291 Å, and the close Pt–Pt interactions give rise to significant fluorescent and phosphorescent behaviour.[97] Each $[Pt_2Ag_4(C{\equiv}CC_6H_4\text{-}3\text{-}OMe)_8]$ cluster is rotated 43.8(5)° along the chain; however, this is most likely due to the steric interactions of the bulky ligands rather than from orbital interactions between adjacent ligands as observed in the TCP complexes. The small metal ions intercalate between parallel acetylide ligands on adjacent platinum complexes and play an important role in charge balance and the stabilization of the stacking interaction. The small metal cations therefore serve a similar stabilizing role to that of small molecules in the TCP and BOP complexes. Synthesis of unsupported platinum acetylide complexes has been accomplished, but the use of $n\mathrm{Bu_4N^+}$ cations prevents close Pt–Pt interaction.[98,99] Acetylide ligands with multiple alkyne bonds such as $[\mathrm{Pt(C{\equiv}C{-}C{\equiv}C{-}R)_4}]^{2-}$ in conjunction with small cations may allow for closer metal–metal interactions and the formation of stacked polymers.

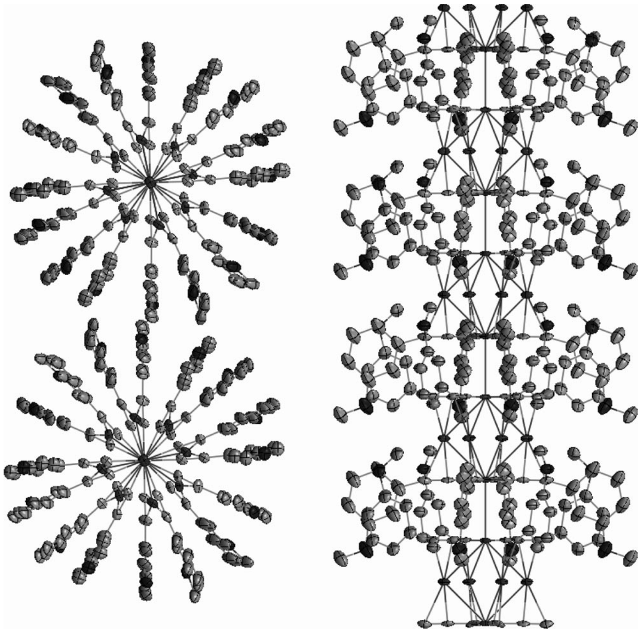

Figure 3. Structure of $[\mathrm{Pt_2Ag_4(C{\equiv}CC_6H_4\text{-}3\text{-}OMe)_8}]_\infty$ as viewed along the *a* (left) and *b* axes (right).

Overall, experimental studies have demonstrated that organometallic platinum complexes possess short Pt–Pt distances which may be attributed in part to the strong π-acidity of the acetylide, isocyanide, and cyanide ligands.[22] While the presence of small molecules may assist in stabilizing the columnar structure, the inability to incorporate more diverse counterions without disrupting the Pt–Pt bonding suggests that combinations of the above ligands in heteroleptic or platinum double salt (PDS) configurations offers the best opportunities to engineer the material properties. Significant progress in the use of PDS systems for sensors has been accomplished by Mann and co-workers.[100–103]

Complexes with Pt–N Bonds

Platinum complexes with nitrogen bound ligands are one of the most common classes of platinum compounds. The use of Cisplatin™ in cancer therapies has led to a large library of heteroleptic platinum complexes based on analogous motifs. Homoleptic [Pt–N$_4$] complexes have also been well studied; however, many of these complexes form dimeric systems rather than polymeric structures.[104,105] Polymers of $([\mathrm{Pt(en)_2}][\mathrm{Pt(en)_2X_2}])^{4-}$ (X = Cl, Br, I) have also been extensively studied, but do not possess short Pt–Pt distances.[106–108] Caseri and co-workers have done significant work on the functionalization of Magnus' green salts $[\mathrm{Pt(NH_2{-}R)_4}][\mathrm{PtCl_4}]$.[109–111] These studies have significantly improved the solubility and optical properties of these complexes whilst retaining short Pt–Pt distances; however, these platinum double salt (PDS) systems are outside the scope of this review.

Glyoximato and Quinone Dioximato Ligands

Platinum(II) complexes with glyoximato and quinone dioximato ligands are an informative contrast to the TCP based complexes. The absence of significant inter-chain hydrogen bonding and the lack of charge balancing cations or anions permit a simpler study of the steric and other contributions of the ligands to the Pt–Pt stacking. The X-ray crystal structure of bis(glyoximato)platinum(II) [Pt(gly)$_2$] was first reported by Ferraris and Viterbo and displayed a Pt–Pt distance indicative of little interaction between the platinum centres (3.5039 Å) (see Figure 4 and Table 2).[112] By contrast, the crystal structure of [Pt(dmg)$_2$] (dmg = dimethylglyoximato) was determined by Frasson et al. and the Pt–Pt distance is substantially shorter [3.23(1) Å]. Schlemper and co-workers reported the metal–metal distance of [Pt(dmg)$_2$] to be 3.25 Å.[113,114] Replacement of dimethylglyoximate with diethylglyoximate ligands leads to a greater Pt–Pt separation with steric interactions between the bulky ethyl groups preventing closer approach.[115]

The ability to prepare thin films of [Pt(dmg)$_2$] and other glyoximate derivatives by sublimation has allowed the material and spectroscopic properties of these complexes to be studied in significant detail.[116–118] Structural characterization of a series of platinum glyoximato complexes demonstrates the relationship between the UV/Vis spectra and the Pt–Pt distance, which is consistent with the correlation previously noted by Yersin and Gliemann.[119] Shorter Pt–Pt distances give rise to a red shift in the absorption maxima, analogous to that observed for the TCP complexes. Kamata et al. have reported a similar correlation between the metal–metal distances and the third order nonlinear optical bulk susceptibility values (χ^3) in thin films of a series of platinum glyoximato complexes.[120,121] This effect can be attributed to electron delocalization under the laser irradiation. The diversity of the bulk material can be enhanced by the co-evaporation of more than one platinum glyoximato complex. Co-evaporation of differing ratios of [Pt(dmg)$_2$] and [Pt(deg)$_2$] gave rise to thin films with new absorption maxima in proportion to the relative ratio of the precursors.[122,123] The measured UV/Vis absorptions and χ^3 values correspond to the ratio of [Pt(dmg)$_2$] to [Pt(deg)$_2$] and

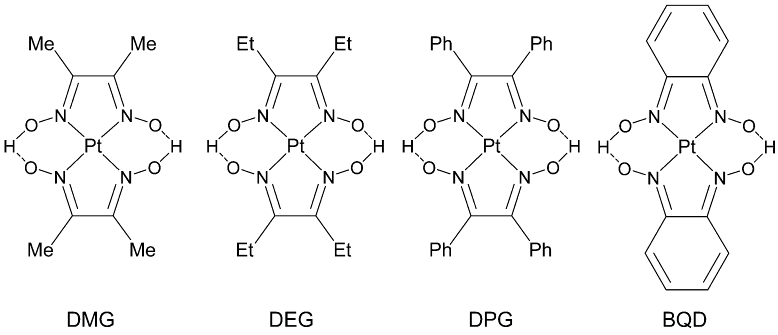

Figure 4. Structure of bis(dimethylglyoximato)platinum(II) (DMG), bis(diethylglyoximato)platinum(II) (DEG), bis(diphenylglyoximato)platinum(II) (DPG), and bis(1,2-benzoquinone dioximato)platinum(II) (BQD) complexes.

Table 2. Platinum–platinum bond lengths in glyoximato and dioximato complexes.

Complex	Pt···Pt distance [Å]	Reference
$[Pt(gly)_2]$	3.5039	[112]
$[Pt(dmg)_2]$	3.23(1) 3.256(3)	[113,114]
$[Pt(deg)_2]$	3.55	[115]
$[Pt(mgl)_2]$[a]	3.24	[133]
$[Pt(emg)_2]$[b]	3.4	[134]
$[Pt(dpg)_2]$ (red form)	3.50	[125]
$[Pt(dpg)_2]$ (green form)	≈ 3.3	[125]
α form $[Pt(bqd)_2]$	3.173	[135]
β form $[Pt(bqd)_2]$	3.69	[136]
γ form $[Pt(bqd)_2]$	3.28	[136]

[a] mgl = 3-methylglyoximato. [b] emg = ethylmethylglyoximato.

indicated that a new material with a combination of Pt–Pt distances was being prepared. The epitaxial growth of a mixture of $[Pt(dmg)_2]$ and $[Pd(dmg)_2]$ has also been demonstrated to give rise to a homogeneous film.[121,124] In this system the UV/Vis absorption maxima could be varied between that of pure $[Pd(dmg)_2]$ (443 nm) and $[Pt(dmg)_2]$ (599 nm). Powder X-ray diffraction demonstrated that the films were homogeneous as opposed to "islands" of $[Pt(dmg)_2]$ and $[Pd(dmg)_2]$. Multiple alternating layers of $[Pt(dmg)_2]$ and $[Pd(dmg)_2]$ could also be synthesized, leading to the possibility of creating heterojunctions. In certain cases the molecular structure can be modified in situ, with the orthorhombic crystalline structure of $[Pt(dmg)_2]$ converted to an amorphous state upon treatment with iodine vapour and subsequently regenerated upon heat treatment.[125] This provides for a method for control over the material properties.

The complex $[Pt(dpg)_2]$ (dpg = diphenylglyoximato) has a relatively long Pt–Pt distance of 3.50 Å in the stable "red form".[126] This effect is understandable given the greater degree of steric interactions between the bulky phenyl groups. By control of the deposition rates, Kamata and coworkers were able to synthesize thin films of a metastable "green form" of $[Pt(dpg)_2]$ on alkali-halide substrates.[127] The green form is orientated by interaction with the substrate into a tetragonal structure which permits closer stacking of the individual complexes, and may be converted into the orthorhombic red form upon heat treatment.[121] This shift in the absorption maxima and the observation of third order nonlinear susceptibilities enhanced by two orders of magnitude are indicative of shorter Pt–Pt distances and single area electron diffraction (SAED) measurements indicate a platinum–platinum distance of about 3.3 Å.[120,125] Comparable changes in the Pt–Pt stacking on different substrates have not been observed for $[Pt(dmg)_2]$. Powder X-ray diffraction studies of $[Pt(dpg)_2]$ at pressures of up to 10 GPa have been carried out and show a monotonic relation between the applied pressure and the Pt–Pt distance along the stacking axis. At 10 GPa, the Pt–Pt distance of $[Pt(dpg)_2]$ decreased significantly to 2.80 Å. Changes in the electrical conductivity and UV/Vis and Raman spectra properties all correlated with the applied pressure.[128–130] Similar effects are observed for $[Pt(dmg)_2]$.[131] The relationship between the prominent UV/Vis absorption maxima and applied pressure has led to the possibility of platinum glyoximato complexes being employed as barochromic sensors. Ohta et al. have extended this concept by synthesizing a series of $[Pt(dpg)_2]$ complexes with long alkoxy chains (n = 4–14) to produce a series of liquid crystals that display temperature-dependent colour changes.[132] Although the Pt–Pt distances could not be measured by single-crystal X-ray diffraction, the complexes showed strong thermochromic dependencies that were considered indicative of changes in the stacking interactions. The interactions between neighbouring platinum complexes are modulated by the van der Waals interaction between neighbouring alkoxy chains that decrease with increasing temperature.

The complex $[Pt(bqd)_2]$ (bqd = 1,2-benzoquinone dioximato) possesses a shorter Pt–Pt distance than any of the glyoximato complexes (3.173 Å).[135] The bqd ligand not only demonstrated less steric interaction, but is a stronger π-acid than the glyoximato ligands, favouring Pt–Pt bond formation. Thin films of $[Pt(bqd)_2]$ formed by vacuum deposition have been investigated by a number of different methodologies.[137,138] Anomalous absorption peaks in the spectra of $[Pt(bqd)_2]$ were observed for thin epitaxially grown films on an NaCl substrate; however, the expected absorption spectra could be obtained upon heating the films to 170 °C.[139] Growth of $[Pt(bqd)_2]$ on a variety of alkali halide substrates in conjunction with high-resolution tunnelling electron microscopy (HRTEM) and SAED observations indicated the formation of a new β phase of [Pt(bqd)$_2$] with a Pt–Pt distance of 3.69 Å. A novel γ phase with an interplanar spacing of 3.28 Å was also observed on a KI substrate with the molecular planes oriented perpendicular to the film surface.[136] Scanning probe and scanning tunnelling microscopy techniques have also been used to characterize the thermal transformation of the β form of [Pt(bqd)$_2$] to the α form,[140] which occurs due to the lower "misfit value" of the α form on the KCl substrate.[141] Scanning tunnelling spectroscopy (STS) and STM have also been used to characterize very thin films (< 10 nm) of [Pt(bqd)$_2$].[140] The individual platinum units of the α form are visible, and the resistivity values are comparable to that of the bulk material.[142] As with [Pt(dpg)$_2$], increasing pressure leads to a decrease in resistivity with an insulator to metal transition at around 0.8 GPa as individual platinum units overlap to a greater extent.[131] Powder X-ray diffraction studies as well as observations of the absorption and polarized reflectance spectra at high pressures confirmed this transition.[143,144] At room temperature and pressure, Sakai et al. have constructed *n*-type field-effect transistors (FETs) with large mobilities from single crystals of [Pt(bqd)$_2$].[145] [Pd(bqd)$_2$] also contains relatively short metal–metal interactions (3.189 Å) and may form homogeneous thin films upon co-evaporation with [Pt(bqd)$_2$], although this has not yet been reported in the literature.

Materials based upon platinum phthalocyanine complexes have a rich history, including the first electron microscope observations of lattice defects and induced radiation damage.[146,147] Although these materials display interesting non-linear optical properties,[148] the large Pt–Pt distance (α phase: 3.81 Å, γ phase: 3.969 Å) suggest minimal overlap of adjacent d_{z^2} orbitals.[149,150] Future studies involving substitution on the phthalocyanine ring may allow for increased solubility and reduction of the Pt–Pt distance.

Unlike the TCP complexes the glyoximato- and (quinone dioximato)platinum complexes do not possess substantial intermolecular hydrogen bonding, nor do these complexes contain ions or solvent molecules that influence the stacking interactions. These relatively uncomplicated polymeric structures may simplify the understanding of the effect of ligands on the platinum stacking interactions. It is therefore surprising to observe a relative lack of structural diversity, with studies focusing on the well known [Pt(dmg)$_2$] and [Pt(bqd)$_2$] complexes. The synthesis of dioximato ligands with phenanthrene or phenanthroline moieties is one potential example (see Figure 5). Other quinone complexes that may give rise to unique quinone dioxime ligands with positive ligand orbital overlap include 1,2-acenaphthylenequinone and 1,2-naphthoquinone. Combining these materials via sublimation may potentially lead to new devices.

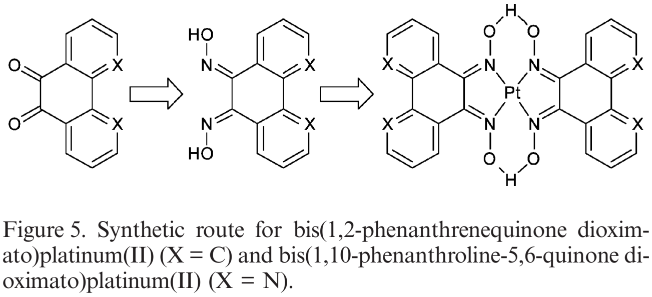

Figure 5. Synthetic route for bis(1,2-phenanthrenequinone dioximato)platinum(II) (X = C) and bis(1,10-phenanthroline-5,6-quinone dioximato)platinum(II) (X = N).

Phenylenediamine, Bipyridyl and Phenanthroline Ligands

The synthesis of homoleptic d^8 metal complexes with the 1,2-phenylenediamine has played an important role in the understanding of the electron transfer in transition metal complexes.[151] Oxidation of the bis(phenylenediamine)metal complexes gives rise to the imine derivative and the new complexes display interesting optical and EPR spectra.[152] (see Figure 6) The synthesis and crystal structure of bis(*o*-phenylenediamine)platinum(II) has been reported, although no close Pt–Pt interactions exist.[105] This complex may be converted into the bis(*o*-semibenzoquinone diimine)platinum(II) complex by alteration of the pH, but despite favourable steric and electronic factors for polymer formation, the bis(*o*-semibenzoquinone diimine)platinum(II) complex forms only a dimeric unit with an unsupported Pt–Pt bond of 3.0109(4) Å. The affinity for the complex to form a stable dimer in preference to polymeric species has been observed in other platinum semibenzoquinone diimine complexes.[153] In contrast, [Pt(en)$_2$]Cl$_2$ does not display any short Pt–Pt contacts despite favourable steric factors, demonstrating the importance of additional back bonding to stabilize the Pt–Pt interactions.[154]

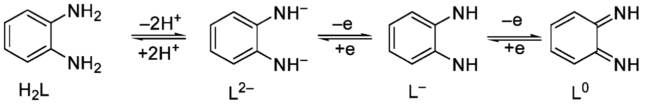

Figure 6. Oxidation and reduction behaviour of the *o*-phenylenediammine ligand (adapted from Konno et al.[105]).

The formation of homoleptic platinum polymers with bipyridyl (bipy) and phenanthroline (phen) ligands may seem unlikely due to the steric repulsion of the ligands around the square-planar geometry. Nevertheless Palmans et al. have reported the synthesis and characterization of a polymer of [Pt^{I}(bipy)$_2$](NO$_3$)·2H$_2$O with a Pt–Pt distance of 3.563 Å.[155] Although this distance indicates only weak metal–metal interaction, it is nevertheless considerably shorter than in the precursor complex [Pt^{II}(bipy)$_2$](NO$_3$)$_2$·2H$_2$O (Pt–Pt > 5 Å). In the simplest method, dark-green needles were formed when an acidic, deaerated solution of [Pt^{II}(bipy)$_2$](NO$_3$)$_2$·2H$_2$O was placed in contact with an iron wire. Electrochemical synthesis of identical needles was also possible. XPS, XANES and elemental analysis provided evidence for the in situ reduction of Pt^{2+} to Pt^{1+}, and the high conductivity parallel but not perpendicular to the Pt–Pt axis is also indicative of significant Pt–Pt bond overlap despite the long intermolecular distance. Crystallographic studies indicate that unlike many other platinum polymers, the individual [Pt^{I}(bipy)$_2$]$^+$ units are not rotated relative to adjacent units, suggesting that the interaction is primarily through the platinum 5d_{z^2} orbitals and not through interaction of the bipyridyl ligands. The distortion of the bipy ligands away from a true square-planar geometry is seen in the crystal structure and allows the ligands to avoid unfavourable steric interactions. The tubular nature of the dark green crystals of $[Pt^{I}(bipy)_2](NO_3)\cdot 2H_2O$ strongly suggests that the growth of the crystals occurs through reduction of Pt^{II} to Pt^{I} at the leading edge of the crystal, with a zone depleted in the precursor material giving rise to the hollow interior.

The ability for a $[Pt^{I}(bipy)_2]^+$ complex to form an interacting platinum chain suggests that other well-known platinum complexes may also possess weak but significant Pt–Pt interactions. For example, in aqueous solutions of $[Pt(phen)_2]^{2+}$ (phen = 1,10-phenanthroline) filamentous material was observed to form upon the surface of electrodes, but was not able to be isolated or identified.[156] The greater rigidity of the 1,10-phenanthroline ligand likely prevents the twisting observed in the $[Pt^{I}(bipy)_2]^+$ system. Introduction of 5,6-dihydro-1,10-phenanthroline or 5,6-epoxy-5,6-dihydro-1,10-phenanthroline ligands may provide the necessary structural flexibility for the formation of isolable platinum polymers (see Figure 7).

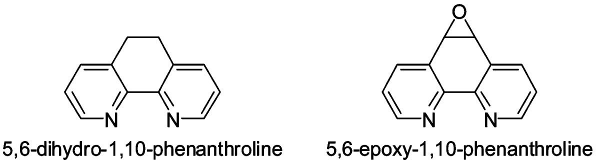

Figure 7. Flexible ligands based upon a bidentate 1,10-phenanthroline unit.

Significant characterization of Pt^{II} complexes with homoleptic nitrogen donor ligands has been undertaken. Nevertheless, much of this work has focused on the dimethylglyoximato and benzodioximato ligand systems. Given the great range of simple and complex ligands that may be synthesized utilizing bipyridyl, phenanthroline and terpyridine ligands many new one-dimensional platinum polymers with unique properties may be possible. Attempts to form polymers with short Pt–Pt distances via oxidation have tended to favour the formation of dimeric complexes.

Complexes with Pt–O Bonds

Since Pt^{II} displays pronounced "soft acid" behaviour, it is not unexpected that relatively fewer complexes are known with oxygen donor ligands and that many of these complexes are unstable. This is reflected in the relative weakness of the platinum–oxygen bond (392 kJ mol^{-1}) compared to the platinum–carbon (598 kJ mol^{-1}) bond.[157] The proclivity for oxygen donors to be displaced by "softer" ligands makes the synthesis of platinum–oxygen complexes more difficult, but nevertheless several different homoleptic platinum–oxygen complexes have been reported and characterized (see Figure 8).

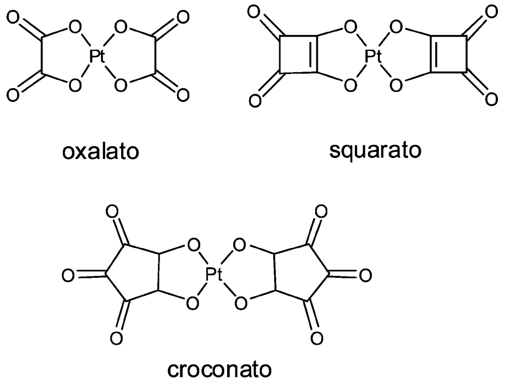

Figure 8. Structure of bis(oxalato)platinate(II) (BOP), bis(squarato)-platinate(II) and bis(croconato)platinate(II) complexes.

Oxalato Ligands

The tendency for bis(oxalato)platinate(II) (BOP) complexes to form long needle-like crystals was first observed over 100 years ago.[1,158] However, the unique conduction properties of the partially oxidized BOP complexes was reported much later by Krogmann and Dodel in 1969.[20,21] Early work in this area including chemical and electrochemical syntheses, conductivity measurements, and examination of the Peierls superstructure has been summarized by Miller and others.[16,159–161] Since this time, further research on new salts of the BOP anion have yielded additional information regarding the relationship between the internal structure and physical properties, including electrical conductivities, of the BOP complexes.

The partially oxidized BOP complexes typically display longer Pt–Pt distances (see Table 3) in comparison to the TCP complexes due to oxalate being a weaker π acid ligand than cyanide.[22,34] Previous work has focused exclusively on the use of transition metal cations and the formation of partially oxidized polymers with very short ($\leq$2.9 Å) Pt–Pt distances.[162] Unlike the TCP complexes, the BOP complexes are amenable to the introduction of a variety of inorganic and organic counter-cations without loss of the short Pt–Pt interactions. Mizuno et al. demonstrated that the $[NH_4]^+$ cation in $[NH_4]_{1.6}[Pt(C_2O_4)_2]$ could be systematically replaced with either $[NH_3Me]^+$, $[NH_2Me_2]^+$, $[NHMe_3]^+$ or $[NMe_4]^+$.[163] In the above series of complexes, neither the increasing size of the ligand nor the increasing pK_a significantly alters the short Pt–Pt bond length (2.80–2.89 Å). This was a key result as it demonstrated the feasibility of introducing a wide array of organic counter-cations. Divalent organic cations have also been incorporated without disruption of the Pt–Pt orbital overlap as in the example of $[H_3NCH_2CH_2NH_3]_{0.8}[Pt(C_2O_4)_2]\cdot 2H_2O$ and $[DEPZ]_{0.9}[Pt(C_2O_4)_2]$ (DEPZ = 1,4-diethylpyrazinium).[164,165] Our group was able to synthesize a one-dimensional platinum polymer incorporating the large planar *N*-methylisoquinolinium cation $[C_{10}H_{10}N]^+$ resulting in the partially oxidized complex $[C_{10}H_{10}N]_{1.6}[Pt(C_2O_4)_2]\cdot 3H_2O$ with a Pt–Pt distance of 2.81 Å.[166] Our attempts to incorporate a potassium 18-crown-6 crown ether complex were only partially successful. Although single-crystal X-ray diffraction indicated that the $[Pt(C_2O_4)_2]^{2-}$ anions do stack, the distances between adjacent platinum centres was 7.811 Å; much too far to indicate any Pt–Pt interactions (see Figure 9). Attempts to generate a complex with shorter Pt–Pt distances by partial oxidation were unsuccessful.

Table 3. Platinum–platinum bond lengths in bis(oxalato), bis(squarato)- and bis(croconato)platinate(II) complexes.

Complex	Pt–Pt Distance [Å]	Ref.
$[NH_4]_{1.69}[Pt(C_2O_4)_2]\cdot H_2O$	2.83	[171]
$[NMeH_3]_{1.71}[Pt(C_2O_4)_2]\cdot H_2O$	2.89	[163]
$[NMe_2H_2]_{1.61}[Pt(C_2O_4)_2]$	2.81	[171]
$[Me_3NH]_{1.59}[Pt(C_2O_4)_2]$	2.80	[163]
$[Me_4N]_{1.65}[Pt(C_2O_4)_2]$	2.81	[163]
$[H_3NCH_2CH_2NH_3]_{0.8}[Pt(C_2O_4)_2]\cdot 2H_2O$	2.82	[164]
$[DEPZ]_{0.9}Pt(C_2O_4)_2$	n/a	[165]
$[C_{10}H_{10}N]_{1.6}[Pt(C_2O_4)_2]\cdot 3H_2O$	2.81	[166]
$[C(NH_2)_3]_2[Pt(C_2O_4)_2]$	3.5876(7)	[172]
$[C(NH_2)_3]_{1.61}[Pt(C_2O_4)_2]\cdot H_2O$	n/a	[173]
$[Cu(en)_2]_2[Pt(C_2O_4)_2]$	3.554 3.855	[174]
$[Cu(en)_2]_{0.80}[Pt(C_2O_4)_2]\cdot 2H_2O$	2.83	[169,170]
$[Pt(en)_2]_{0.80}[Pt(C_2O_4)_2]\cdot 2H_2O$	2.82	[169,170]
$[Ag(NH_3)_2]_2[Pt(C_2O_4)_2]$	3.5857(11)	[175]
$[Cu(bipy)(H_2O)_n]_6[Pt(C_2O_4)_2]_7\cdot 7H_2O$	2.848	[176]
$[Cu(bipy)(H_2O)_n]_8[Pt(C_2O_4)_2]_{10}\cdot 8H_2O$	3.0082	[176]
$K_{1.2}(H_3O^+)_{0.5}[Pt(C_5O_5)_2]$	3.12	[177]

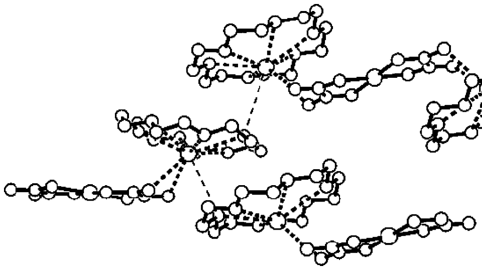

Figure 9. ORTEP plot of $[K(18\text{-crown-}6)]_2[Pt(C_2O_4)_2]$ at 50% probability level.

The ability to incorporate divalent metal cations or transition metal complexes without disrupting the short Pt–Pt distances is a feature that occurs in partially oxidized BOP salts but not in partially oxidized TCP complexes. Krogmann reported a partially oxidized calcium BOP salt having the formula $Ca_{0.84}[Pt(C_2O_4)_2]\cdot 4H_2O$ with a Pt–Pt distance of 2.876 Å, however no further information about this complex is available.[167] Mizuno synthesized a new form of the calcium BOP salt having formula, $Ca_{0.756}[Pt(C_2O_4)_2]\cdot 3H_2O$ and a Pt–Pt bond length of 2.89(1) Å and with a triclinic structure, similar to that of $Cu_{0.84}[Pt(C_2O_4)_2]\cdot 7H_2O$.[168] Although $Ca_{0.756}[Pt(C_2O_4)_2]\cdot 3H_2O$ had an average conductivity value in the same range as other partially oxidized BOP salts (7.4 Ω^{-1} cm^{-1}), its degree of partial oxidation and Pt–Pt bond length was much higher than other partially oxidized BOP salts containing divalent cations. The instability of $Ca_{0.756}[Pt(C_2O_4)_2]\cdot 3H_2O$ suggests that analogous to the $[Pt(bqd)_2]$ complex, a variety of secondary phases may be isolated under exceptional circumstances. Mizuno also reported a series of complexes with $[M(en)_2]_{0.80}[Pt(C_2O_4)_2]\cdot 2H_2O$ (M = Cu or Pt, en = ethylenediammine). Both salts have similar crystal structures with nearly identical Pt–Pt spacings (2.82–2.83 Å for both salts).[169,170]

The use of large counter cations seem to have little effect on either the degree of partial oxidation or stacking of the BOP moieties, but represent a significant shortening from the divalent parent complex $[Cu(en)_2]_2[Pt(C_2O_4)_2]$ where the Pt–Pt distances are 3.554 and 3.855 Å.[174] In a similar synthesis, Yamamoto et al. reacted $K_{1.6}[Pt(C_2O_4)_2]\cdot 2H_2O$ with $[Cu(bipy)(H_2O)_3](NO_3)_2$ to yield $[Cu(bipy)(H_2O)_n]_6[Pt(C_2O_4)_2]_7\cdot 7H_2O$ (*n* = 2, 3, 4; where platinum has an average oxidation number of +2.29) and $[Cu(bipy)(H_2O)_n]_8[Pt(C_2O_4)_2]_{10}\cdot 8H_2O$ (*n* = 3, 4; where platinum has an average oxidation number of +2.40).[176] The crystal structure of $[Cu(bipy)(H_2O)_n]_6[Pt(C_2O_4)_2]_7\cdot 7H_2O$ (*n* = 2, 3 or 4) is quite interesting in that an oxygen from the platinum-chelated oxalato ligand is directly coordinated to the paramagnetic cation centre yet there is no direct interaction between the anionic chains. The average Pt–Pt distance between the seven platinum ions within the anionic chain was reported as 2.848 Å with the shortest distance between two monomers being 2.762 Å. In Yamamato's analysis of $[Cu(bipy)(H_2O)_n]_8[Pt(C_2O_4)_2]_{10}\cdot 8H_2O$ (*n* = 3 or 4), no such coordination of the cation to the oxalate oxygen atoms exists. The conductivity of these two compounds is vastly different as well with the former reported as 0.5–0.9 $\Omega^{-1}\,cm^{-1}$ and the latter being $1.3 \times 10^{-3}\ \Omega^{-1}\,cm^{-1}$.

Despite the significant study of BOP salts, much remains unknown about the mechanisms whereby BOP salts are partially oxidized to oligomeric systems. During Krogmann's initial studies on the partial oxidation of $K_2Pt(C_2O_4)_2\cdot 2H_2O$, four distinct UV/Vis absorbances were reported. These peaks were attributed to the formation of variably sized $[Pt(C_2O_4)_2]_n$ oligomers. Keller et al. derived a mechanism for the formation of the higher order $[Pt(C_2O_4)_2]_n$ oligomers by using controlled chemical oxidation of $K_2Pt(C_2O_4)_2\cdot 2H_2O$ in 2.0 M CF_3SO_3H with Ce^{4+} as an oxidant.[178] This resulted in the appearance of four absorbance maxima at 426, 510, 600 and 680 nm, in agreement with those originally reported. By varying the concentration, pH, and the amount of oxidant used, the relative intensities of the peaks could be adjusted. At pH 2.5, the addition of 1 electron equivalent of oxidant led to the appearance of the 426 nm absorbance maxima attributed to the formation of a dimeric bis(oxalato)platinate(III) $[Pt^{3+}(C_2O_4)_2]_2^{2-}$ species. This presence of this complex was also confirmed by ^{195}Pt NMR spectroscopy. This species was found to be unstable above a pH of 2.0, which led to disproportionation into $[Pt^{II}(C_2O_4)_2]^{2-}$ and $[Pt^{IV}(C_2O_4)_2]$. Below pH 2.0, the dimer was stable in solution for up to three days. Varying the pH of the $K_2Pt(C_2O_4)_2\cdot 2H_2O$ solution at or below 2.5, addition of oxidant led to the appearance of the 426 nm $[Pt^{3+}(C_2O_4)_2]_2^{2-}$ species as well as the 510, 600 and 680 nm absorbances associated to the formation of $[Pt^{2.67+}(C_2O_4)_2]_3^{4-}$, $[Pt^{2.5+}(C_2O_4)_2]_4^{6-}$ and $[Pt^{2.4+}(C_2O_4)_2]_5^{8-}$ respectively. Ultimately it has been hypothesized that H^+ ions play a critical role in the formation of higher oligomers through the initial stabilization of the polyanionic platinum chain. Pentamers of $[Pt^{2.4+}(C_2O_4)_2]_5{}^{8-}$ are the shortest oligomers over which the average oxidation state of the polymer ($Pt^{2.4+}$) is observed. The pentamer is also the shortest oligomer over which Peierls distortion may be observed, due to the 4/5 filling of the conduction band. This may explain the inability to observe hexamers in solutions, and suggests that growth of longer polymers may occur via aggregation of the pentamer units.

Work on new, non-partially oxidized BOP salts has continued well into this decade. Sakai et al. published results from the characterization of a bisguanidium bis(oxalato)-platinate(II) $(CH_6N_3)_2[Pt(C_2O_4)_2]$ as well as the double platinum, bis(2-aminopyridine)(2,2′-bipyridine)platinum(II) bis(oxalato)platinate(II) dihydrate $[Pt(C_{10}H_8N_2)(C_5H_6N_2)_2]$-$[Pt(C_2O_4)_2]\cdot 2H_2O$ salt.[172,179] Neither of these complexes demonstrated significant Pt–Pt overlap, although X-ray analysis shows that the guanidinium cation stabilizes the overall structure via hydrogen bonding between the organic cation and both the chelating and carbonyl oxygen's contained in the oxalate ligands. Recent work indicates that the bisguanadinum BOP complex may be partially oxidized leading to a reduction in the average Pt–Pt distance.[173] Wu and co-workers have synthesized and characterized $[Ag(NH_3)_2]_2$-$[Pt(C_2O_4)_2]$ which displays a stacking distance along the Pt–Pt axis of 3.5857(11) Å (see Figure 10). The long distance between platinum centres and the 0° rotation between $[Pt(C_2O_4)_2]^{2-}$ units suggests little if any significant interaction between the adjacent platinum units. Band structure calculations on $Mg_{0.82}[Pt(C_2O_4)_2]\cdot 5.3H_2O$ have been performed by Nayak et al. which illustrate the relationship between Pt–Pt distance and the degree of partial oxidation.[180] The preferred rotation between adjacent bis(oxalato)platinate units was shown to be either 45° or 60° in systems containing more than two platinum units. The 60° conformation is only 1.9 kcal mol^{-1} lower in energy than the 45° orientation, and the resulting "staircase arrangements" are in agreement with experimentally observed results.

Figure 10. ORTEP plot of $[Ag(NH_3)_2]_2[Pt(C_2O_4)_2]$ at 50% probability level generated from the data deposited with the CSD.

With the use of a novel slow diffusion method, Sakai was able to grow single crystals of $[Pt(C_{10}H_8N_2)(C_5H_6N_2)_2]$ $[Pt(C_2O_4)_2]\cdot 2H_2O$.[179] X-ray analysis of this one-dimensional Magnus' green salt-like compound showed strong interactions between the platinum ion pairs due to π–π stacking between the 2,2′-bipyridine and oxalate ligands, but weaker interactions between the alternating ion pairs. The intramolecular or cation-anion pair Pt–Pt bond length was reported as 3.9294(6) Å whereas the intermolecular or Pt–Pt bond length between two adjacent Pt ion pairs reported as 5.0302(7) Å. Both lengths indicate the lack of interactions between the $5d_{z^2}$ orbital on the platinum. It is noteworthy that within the platinum cation, the monodenticity of the 2-aminopyridine ligands allows for perpendicular orientation with respect to the bidentate 2,2′-bipyridine ligand limiting the minimum Pt–Pt stacking distance. The 2-aminopyridine ligands extend well above and below the stacking plane which leads to measured distances of 3.46(1) Å and 3.41(7) Å between the intra- and inter-ion pairs, respectively.

The unique properties of the BOP salts enable them to be used for the formation of other novel materials. Xu et al. demonstrated that a glassy carbon working electrode could be modified to form a microelectrode array by the growth of nanowires of $K_{1.6}[Pt(C_2O_4)_2]$.[181] Cyclic voltammetry and chronoamperometry experiments demonstrated that the growth of the partially oxidized "nano-electrodes" is a two step, diffusion controlled process with growth of the platinum polymer occurring via addition of BOP monomers.[182,183] Recent work from our group has demonstrated the ability to synthesize the partially oxidized BOP polymers within constricted geometries.[173] Use of porous anodic alumina oxide filters as growth templates allows for the constriction of the polymer diameter to 20 nm while retaining their full electrical conductivity. More recently we have demonstrated that micron-sized, hollow tubes of $X_{0.8}Pt$ may be formed by the reductive pyrolysis of $X_{0.8}[Pt(C_2O_4)_2]$ (X = Co, Fe, Ni) (see Figure 11).[184] These partially oxidized BOP salts may be reduced under a hydrogen atmosphere at 120 °C to form bimetallic alloys whilst retaining their structure, and these materials may have catalytic applications. The homogeneity of platinum and the co-metal in the final structures was confirmed by energy-dispersive X-ray spectroscopy (EDS). The hollow geometry may be due to rapid growth of the stacked polymers at high voltages leading to the formation of a depletion zone within the growing structure, or to changes in the internal structure upon pyrolysis. The complex $Ag_2[Pt(C_2O_4)_2]$ has been demonstrated to be a suitable precursor for the synthesis of nanoparticles of a silver-platinum alloy, and this preliminary work indicates that this method is more general.[185]

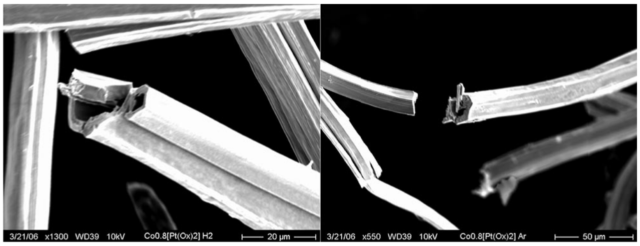

Figure 11. SEM images of hollow structures of $Co_{0.8}[Pt(C_2O_4)_2]$ after reduction under a hydrogen atmosphere.

BOP complexes display greater versatility than TCP complexes due to the ability to incorporate a larger range of cations that allow for modification of the physical properties, including Pt–Pt distance. However, as with the TCP complexes the columnar Pt–Pt structures are stabilized by additional bonding interactions from water molecules that alter the material properties upon dehydration.

Squarate and Crocoanate Ligands

The successful synthesis and characterization of numerous bis(oxalato)platinate salts has led to the investigation of other bidentate-oxo ligands with planarity similar to that of oxalic acid. Compared to oxalate, other oxygen bound ligands have received significantly less attention. Toftlund synthesized the bis(squarato)platinate(II) complex $K_2[Pt(C_4O_4)_2]$ and the partially oxidized analogue $K_{1.6}[Pt(C_4O_4)]$ by treating a warm aqueous solution of $[Pt(H_2O)_4]^{2+}$ with squaric acid (see Figure 8).[186] Concentration of the solution gives rise to highly coloured oligomers analogous to those originally reported by Krogmann for the potassium bis(oxalato)platinate complexes.[20,21] ESCA characterization of the anisotropic crystals showed a shift in the platinum binding energy compared to the parent platinum(II) compound indicative of a change in the overall oxidation state. The bis(squarato)platinate complexes were also capable of oligomerization which gave rise to dimeric units of $Ba_2[Pt_2(C_4O_4)_4]\cdot 6H_2O$ with squarato ligands bridging between different platinum centres, analogous to the pyridonato "platinum blue" systems.[187,188] Our studies on the $K_2[Pt(C_4O_4)_2]$ complex indicated that partial oxidation of the $K_2[Pt(C_4O_4)_2]$ salt led to the appearance of a strong absorbance peak at 510 nm, similar to those reported for the formation of oligomers of $[Pt(C_2O_4)_2]^{2-}$ with short Pt–Pt interactions.[178,184] Toftlund has also reported the isolation of the partially oxidized bis(croconato)platinate complex $K_{1.2}(H_3O^+)_{0.5}[Pt(C_5O_5)_2]$.[177,189] Single crystal diffraction studies demonstrated the Pt–Pt distance to be 3.12 Å with each bis(croconato)platinate unit rotated by approximately 45° relative to the adjacent unit. This twisting is analogous to that observed for bis(oxalato)complexes and is indicative of bonding interaction between adjacent units in the chain.[180]

Malonato and Acetylacetonato Ligands

The interaction of electronic and steric effects on the degree of Pt–Pt interaction can be studied by comparison of the bis(malonato)platinate(II) and bis(methylmalonato)platinate(II) complexes (see Figure 12). The bismalonatoplatinate $[Pt(C_3H_2O_4)_2]^{2-}$ and *syn*- and *anti*-bis(2-methylmalonato)platinate $[Pt(C_4H_4O_4)_2]^{2-}$ complexes were formed through reaction of malonic acid and 2-methylmalonic acid with K_2PtCl_4.[190] Chemical oxidization of solutions containing $[Pt(C_3H_2O_4)_2]^{2-}$ using $[(NH_3)_2Ce(NO_3)_4]$ led to the formation of the dimeric tetramalonatodiplatinum(III) species, $[Pt(C_3H_2O_4)_2]_2{}^{2-}$. The putative dimer was short lived; only lasting for 0.5 h. The inability to form a stable multimeric complex was attributed to the steric hindrance caused by the non-planar geometry of the malonate ligands.[178] Formation of transient dimeric species was not observed for the 2-methylmalonato complex $[Pt(C_4H_4O_4)_2]^{2-}$. Stoichiometric addition of $[Pt^{IV}(C_3H_2O_4)_2]$ or $[Pt^{IV}(C_4H_4O_4)_2]$ to solutions of $[Pt^{II}(C_3H_2O_4)_2]^{2-}$ or $[Pt^{II}(C_4H_4O_4)_2]^{2-}$ did not result in the formation of partially oxidized polymeric systems, and attempts to form partially oxidized systems with short Pt–Pt distances through electrochemical oxidation were also unsuccessful. Although the steric increase in the bis(malonato)platinate complex is relatively small compared to the bis(oxalato)platinate systems, the disruption of the π-conjugation and the shift to a weaker π-acceptor ligand likely contributes to the reduction in Pt–Pt interaction.

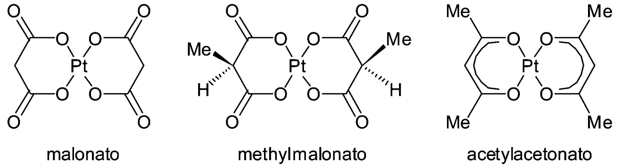

Figure 12. Structure of bis(malonato)platinate(II), *syn*-bis(methylmalonato)platinate(II) and bis(acetylacetonato)platinum(II).

The platinum acetylacetonato (acac) complex $[Pt(C_5H_7O_2)_2]$ has been extensively studied, and although numerous crystal structures exist,[191–193] no short Pt–Pt distances (≤ 3.5 Å) have been observed. Although the complex possesses π-delocalization across the acac ligand which may be expected to favour Pt–Pt interaction, the steric hindrance of the methyl moieties appears to be too unfavourable to allow for close interactions.

The weak affinity of divalent platinum for oxygen ligands has presented an obstacle in the preparation of a wider variety of new types of complexes that can form polymers with short Pt–Pt distances. The need for stable, sterically unhindered, π-acidic ligands has limited the ability to modify the structure of these complexes. A possible extension to the bis(squarato) and bis(croconato) complexes may be the synthesis of the platinum(II) complex based upon rhodozoic acid (see Figure 13).

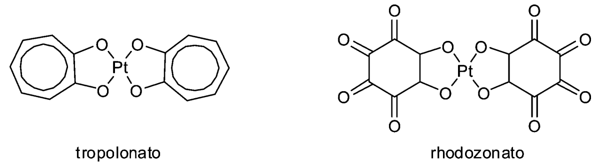

Figure 13. Structure of bis(tropolonato)platinum(II) and bis(rhodozonato)platinate(II).

Our preliminary attempts to synthesize bis(rhodozonato)platinate(II) by reaction of aqueous solutions of K_2PtCl_4 with rhodozoic acid were unsuccessful; however, it may be possible to synthesize this complex through reaction of the ligand with $[Pt(H_2O)_4]^{2+}$. The bis(tropolonato)platinum(II) complex has not been reported either, but the analogous palladium complex is known and has been characterized by single-crystal X-ray diffraction, presenting another complex for future studies.[194]

Conclusions

Polymers of platinum complexes with direct Pt–Pt bonding have significant potential in the development of sensors and other technological applications, and new complexes that display short Pt–Pt distances have opened up fresh avenues for research. This review has attempted to highlight ways in which the molecular diversity may be expanded, and areas in which new advances may be expected. Although the importance of using sterically favourable, strong-field ligands continues to be a guiding principle, unanticipated complexes such as $[Pt^{I}(bipy)_2]^+$ indicate that there are still many factors that are not fully understood. Familiar systems such as those incorporating tetra(cyano)platinate and bis(oxalato)platinate anions allow the exploration of the effect of cation substitution, but are affected by loss of structure upon dehydration, and a limited number of complexes containing glyoximato and quinone dioximato ligands have been well studied for their material properties, and present an unexplored area of research. The short platinum–platinum distance also gives rise to unique luminescent and non-linear optical properties which may be tuned by modification of the stabilizing ligands. From a technological perspective, the use of platinum double salts for vapochromic and bathochromic sensors is currently the most technologically well-developed application. We anticipate that the ongoing work into the synthesis and characterization of new homoleptic platinum complexes will continue to point the way to a deeper understanding of metal–metal interactions in these and other related systems.

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[1] J. W. Döbereiner, *Poggendorffs Ann. Phys.* **1833**, *28*, 180.
[2] R. Mattes, K. Krogmann, *Z. Anorg. Allg. Chem.* **1964**, *332*, 247.
[3] S. Iijima, *Nature* **1991**, *354*, 56.
[4] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho, H. Dai, *Science* **2000**, *287*, 622.
[5] X. Michalet, F. F. Pinaud, L. A. Bentolila, J. M. Tsay, S. Doose, J. J. Li, G. Sundaresan, A. M. Wu, S. S. Gambhir, S. Weiss, *Science* **2005**, *307*, 538.
[6] T. J. Bukowski, J. H. Simmons, *Crit. Rev. Solid State Mater. Sci.* **2002**, *27*, 119.
[7] A. Kolmakov, M. Moskovits, *Annu. Rev. Mater. Res.* **2004**, *34*, 151.
[8] E. Comini, C. Baratto, G. Faglia, M. Ferroni, A. Vomiero, G. Sberveglieri, *Prog. Mater. Sci.* **2009**, *54*, 1.
[9] M. Corso, W. Auwarter, M. Muntwiler, A. Tamai, T. Greber, J. Osterwalder, *Science* **2004**, *303*, 217.
[10] D. Bhaumik, J. E. Mark, *Synth. Met.* **1983**, *6*, 299.
[11] M. Wysocka, K. Winkler, J. R. Stork, A. L. Balch, *Chem. Mater.* **2004**, *16*, 771.
[12] G. M. Finniss, E. Canadell, C. Campana, K. R. Dunbar, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2772.
[13] T. Murahashi, H. Kurosawa, *Coord. Chem. Rev.* **2002**, *231*, 207.
[14] C. H. Chien, J. C. Chang, C. Y. Yeh, G. H. Lee, J. M. Fang, S. M. Peng, *Dalton Trans.* **2006**, 2106.
[15] R. M. Bozorth, L. Pauling, *Phys. Rev.* **1932**, *39*, 537.
[16] J. S. Miller, *Extended linear chain compounds*, vol. 1–3, Plenum Press, New York, **1982**.
[17] R. E. Rundle, *J. Phys. Chem.* **1957**, *61*, 45.
[18] K. Krogmann, *Z. Anorg. Allg. Chem.* **1968**, *358*, 97.
[19] K. Krogmann, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 980.
[20] K. Krogmann, P. Dodel, *Chem. Ber.* **1966**, *99*, 3402.
[21] K. Krogmann, P. Dodel, *Chem. Ber.* **1966**, *99*, 3408.
[22] G. Aullón, S. Alvarez, *Chem. Eur. J.* **1997**, *3*, 655.
[23] T. Ziegler, J. K. Nagle, J. G. Snijders, E. J. Baerends, *J. Am. Chem. Soc.* **1989**, *111*, 5631.
[24] J. B. Cornelius, R. M. Trapp, T. J. Delord, F. R. Fronczek, S. F. Watkins, J. J. Orosz, R. L. Musselman, *Inorg. Chem.* **2003**, *42*, 3026.
[25] R. L. Musselman, *Inorg. Chim. Acta* **2008**, *361*, 820.
[26] L. J. Grove, J. M. Rennekamp, H. Jude, W. B. Connick, *J. Am. Chem. Soc.* **2004**, *126*, 1594.
[27] A. G. Dylla, D. E. Janzen, M. K. Pomije, K. R. Mann, *Organometallics* **2007**, *26*, 6243.
[28] J. Fornies, S. Fuertes, J. A. Lopez, A. Martin, V. Sicilia, *Inorg. Chem.* **2008**, *47*, 7166.
[29] L. J. Grove, A. G. Oliver, J. A. Krause, W. B. Connick, *Inorg. Chem.* **2008**, *47*, 1408.
[30] M. Kato, *Bull. Chem. Soc. Jpn.* **2007**, *80*, 287.
[31] A. Canty, *Comprehensive Organometallic Chemistry III*, vol. 8, *Compounds of Group 10*, vol. 8, 3rd ed., Elsevier, Amsterdam, **2006**.
[32] M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte, R. Eisenberg, *Inorg. Chem.* **2000**, *39*, 447.
[33] C. E. Whittle, J. A. Weinstein, M. W. George, K. S. Schanze, *Inorg. Chem.* **2001**, *40*, 4053.
[34] W. B. Connick, R. E. Marsh, W. P. Schaefer, H. B. Gray, *Inorg. Chem.* **1997**, *36*, 913.
[35] M. Mitsumi, H. Ueda, K. Furukawa, Y. Ozawa, K. Toriumi, M. Kurmoo, *J. Am. Chem. Soc.* **2008**, *130*, 14102.
[36] R. Kato, *Chem. Rev.* **2004**, *104*, 5319.
[37] E. S. Peterson, R. D. Larsen, E. H. Abbott, *Inorg. Chem.* **1988**, *27*, 3514.
[38] D. Min, R. D. Larsen, K. Emerson, E. H. Abbott, *Inorg. Chem.* **1990**, *29*, 73.
[39] E. S. Peterson, D. P. Bancroft, D. Min, F. A. Cotton, E. H. Abbott, *Inorg. Chem.* **1990**, *29*, 229.
[40] J. R. Marvin, E. H. Abbott, *Inorg. Chim. Acta* **1996**, *247*, 267.
[41] D. A. Sartori, J. G. Einerwold, E. H. Abbott, *Inorg. Chim. Acta* **1998**, *268*, 311.
[42] R. E. Rundle, J. H. Sturdivant, *J. Am. Chem. Soc.* **1947**, *69*, 1561.
[43] M. N. Hoechstetter, C. H. Brubaker, *Inorg. Chem.* **1969**, *8*, 400.
[44] W. Knop, *Justus Liebigs Ann. Chem.* **1842**, *43*, 111.
[45] W. Knop, G. Schnedermann, *J. Prakt. Chem.* **1846**, *37*, 461.
[46] K. Krogmann, H. D. Hausen, *Z. Anorg. Allg. Chem.* **1968**, *358*, 67.
[47] K. Krogmann, H. D. Hausen, *Z. Naturforsch. B Teil B* **1968**, *23*, 1111.
[48] K. Krogmann, G. Ringwald, *Z. Naturforsch. B Teil B* **1968**, *23*, 1112.
[49] K. Krogmann, D. Stephan, *Z. Anorg. Allg. Chem.* **1968**, *362*, 290.
[50] J. S. Miller, *Inorg. Chem.* **1976**, *15*, 2357.
[51] J. S. Miller, *Inorg. Chem.* **1977**, *16*, 957.
[52] C. Muhle, J. Nuss, R. E. Dinnebier, M. Jansen, *Z. Anorg. Allg. Chem.* **2004**, *630*, 1462.
[53] C. Mühle, E.-M. Peters, M. Jansen, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2063.
[54] C. Mühle, E.-M. Peters, M. Jansen, *Z. Naturforsch. Teil B* **2009**, *64*, 111.
[55] R. L. Maffly, J. A. Abys, J. M. Williams, R. N. Rhoda, in: *Inorg. Synth.*, vol. 19 (Ed.: F. S. Duward), **1979**, pp. 6.
[56] R. L. Maffly, P. L. Johnson, J. M. Williams, *Acta Crystallogr., Sect. B: Struct. Sci.* **1977**, *33*, 884.
[57] C. Muhle, A. Karpov, M. Jansen, *Z. Naturforsch. Teil B* **2005**, *60*, 1269.

[58] C. Muhle, J. Nuss, M. Jansen, *Z. Kristallogr., New Cryst. Struct.* **2005**, *220*, 528.
[59] A. Loosli, M. Wermuth, H. U. Gudel, S. Capelli, J. Hauser, H. B. Burgi, *Inorg. Chem.* **2000**, *39*, 2289.
[60] D. Shiota, N. Matsushita, *Chem. Lett.* **2008**, *37*, 398.
[61] B. A. Maynard, R. E. Sykora, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2008**, *64*, m138.
[62] K. Sakai, Y. Miyabe, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2004**, *60*, M69.
[63] M. Vavra, I. Potocnak, D. Steinborn, C. Wagner, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, m1895.
[64] T. Akitsu, Y. Einaga, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, m862.
[65] K. Sakai, M. Mizota, N. Akiyama, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2004**, *60*, M88.
[66] G. S. V. Coles, A. E. Underhill, J. M. Williams, A. J. Schultz, *J. Chem. Soc., Dalton Trans.* **1983**, 2529.
[67] G. S. V. Coles, A. E. Underhill, K. Carneiro, *J. Chem. Soc., Dalton Trans.* **1983**, 1411.
[68] G. Gliemann, H. Yersin, in: *Structure and Bonding*, vol. 62, Springer, Berlin, **1985**, pp. 87.
[69] G. F. Needham, P. L. Johnson, J. M. Williams, *Acta Crystallogr., Sect. B: Struct. Sci.* **1977**, *33*, 1581.
[70] L. Ouahab, J. Padiou, D. Grandjean, C. Garrigoulagrange, P. Delhaes, M. Bencharif, *J. Chem. Soc., Chem. Commun.* **1989**, 1038.
[71] R. M. Lobkovskaya, N. D. Kushch, R. P. Shibaeva, E. B. Yagubsky, M. A. Simonov, *Kristallografiya* **1989**, *34*, 1158.
[72] E. I. Zhilyaeva, R. N. Lyubovskaya, S. A. Torunova, S. V. Konovalikhin, O. A. Dyachenko, R. B. Lyubovskii, *Synth. Met.* **1996**, *80*, 91.
[73] A. D. Dubrovskii, N. G. Spitsina, A. N. Chekhlov, O. A. Dyachenko, L. I. Buravov, A. A. Lobach, J. V. Gancedo, C. Rovira, *Synth. Met.* **2004**, *140*, 171.
[74] M. Fettouhi, L. Ouahab, D. Grandjean, L. Toupet, *Acta Crystallogr., Sect. B: Struct. Sci.* **1992**, *48*, 275.
[75] M. Fettouhi, L. Ouahab, D. Grandjean, G. Mousdis, P. Delhaes, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 2141.
[76] M. Fettouhi, L. Ouahab, D. Grandjean, G. Mousdis, P. Delhaes, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1992**, *48*, 1920.
[77] N. B. Wood, *MS Thesis*, Montana State University (Bozeman), **1999**.
[78] T. Kawasaki, L. Jiang, T. Iyoda, T. Araki, D. A. Tryk, K. Hashimoto, A. Fujishima, *Chem. Lett.* **1995**, 879.
[79] T. Kawasaki, L. Jiang, T. Iyoda, T. Araki, K. Hashimoto, A. Fujishima, *J. Phys. Chem. B* **1997**, *101*, 2723.
[80] C. L. Exstrom, M. K. Pomije, K. R. Mann, *Chem. Mater.* **1998**, *10*, 942.
[81] Y. Kunugi, K. R. Mann, L. L. Miller, C. L. Exstrom, *J. Am. Chem. Soc.* **1998**, *120*, 589.
[82] J. S. Miller, D. G. Marsh, *Inorg. Chem.* **1976**, *15*, 2293.
[83] N. G. Connelly, J. G. Crossley, A. G. Orpen, H. Salter, *J. Chem. Soc., Chem. Commun.* **1992**, 1564.
[84] H. Bois, N. Connelly, J. Crossley, J. Guillorit, G. Lewis, A. Orpen, P. Thornton, *J. Chem. Soc., Dalton Trans.* **1998**, 2833.
[85] S. M. Drew, D. E. Janzen, C. E. Buss, D. I. MacEwan, K. M. Dublin, K. R. Mann, *J. Am. Chem. Soc.* **2001**, *123*, 8414.
[86] S. M. Drew, D. E. Janzen, K. R. Mann, *Anal. Chem.* **2002**, *74*, 2547.
[87] C. E. Buss, K. R. Mann, *J. Am. Chem. Soc.* **2002**, *124*, 1031.
[88] P. J. Martellaro, S. K. Hurst, R. Larson, E. H. Abbott, E. S. Peterson, *Inorg. Chim. Acta* **2005**, *358*, 3377.
[89] K. A. Hofmann, G. Bugge, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 1772.
[90] R. Ludwig, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2578.
[91] R. Nast, W.-D. Heinz, *Chem. Ber.* **1962**, *95*, 1478.
[92] M. C. Barral, R. Jimenez, E. Royer, V. Moreno, A. Santos, *Inorg. Chim. Acta* **1978**, *31*, 165.
[93] D. Zhang, D. B. McConville, C. A. Tessier, W. J. Youngs, *Organometallics* **1997**, *16*, 824.
[94] P. F. J. Espinet, F. Martinez, M. Tomas, E. Lalinde, M. T. Moreno, A. J. Ruiz, A. J. Welch, *J. Chem. Soc., Dalton Trans.* **1990**, 791.
[95] J. P. H. Charmant, J. Fornies, J. Gomez, E. Lalinde, R. I. Merino, M. T. Moreno, A. G. Orpen, *Organometallics* **1999**, *18*, 3353.
[96] I. Ara, J. Fornies, J. Gomez, E. Lalinde, M. T. Moreno, *Organometallics* **2000**, *19*, 3137.
[97] B. Gil, J. Fornies, J. Gomez, E. Lalinde, A. Martin, M. T. Moreno, *Inorg. Chem.* **2006**, *45*, 7788.
[98] J. Benito, J. R. Berenguer, J. Forniés, B. Gil, J. Gómez, E. Lalinde, *Dalton Trans.* **2003**, 4331.
[99] Á. Díez, J. Fernández, E. Lalinde, M. T. Moreno, S. Sánchez, *Dalton Trans.* **2008**, 4926.
[100] J. W. Grate, L. K. Moore, D. E. Janzen, D. J. Veltkamp, S. Kaganove, S. M. Drew, K. R. Mann, *Chem. Mater.* **2002**, *14*, 1058.
[101] Y. Kunugi, K. R. Mann, L. L. Miller, C. L. Exstrom, *Vapochromic LED*, U. S. Pat. 6,578,406, **2003**.
[102] Y. Kunugi, K. R. Mann, L. L. Miller, M. K. Pomije, *Vapochromic photodiode* U. S. Pat. 6,137,118, **2000**.
[103] K. R. Mann, C. A. Daws, C. L. Exstrom, D. E. Janzen, M. Pomije, *Vapochromic platinum complexes and salts*, U. S. Pat. 5,766,952, **1998**.
[104] D. Herebian, E. Bothe, F. Neese, T. Weyhermuller, K. Wieghardt, *J. Am. Chem. Soc.* **2003**, *125*, 9116.
[105] Y. Konno, N. Matsushita, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1046.
[106] A. L. Beauchamp, D. Layek, T. Theophanides, *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *38*, 1158.
[107] N. Matsushita, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2006**, *62*, m33.
[108] N. Matsushita, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, m514.
[109] M. Fontana, H. Chanzy, W. R. Caseri, P. Smith, A. P. H. J. Schenning, E. W. Meijer, F. Grohn, *Chem. Mater.* **2002**, *14*, 1730.
[110] M. Fontana, W. R. Caseri, P. Smith, A. P. H. J. Schenning, E. W. Meijer, *Inorg. Chim. Acta* **2003**, *353*, 320.
[111] M. Fontana, W. Caseri, P. Smith, *Platinum Met. Rev.* **2006**, *50*, 112.
[112] G. Ferraris, D. Viterbo, *Acta Crystallogr., Sect. B: Struct. Sci.* **1969**, *25*, 2066.
[113] E. Frasson, C. Panattoni, R. Zannetti, *Acta Crystallogr.* **1959**, *12*, 1027.
[114] M. Sakhawat Hussain, B. E. V. Salinas, E. O. Schlemper, *Acta Crystallogr., Sect. B: Struct. Sci.* **1979**, *35*, 628.
[115] M. Kanakubo, K. Yamamoto, K. Honda, H. Ushijima, T. Kamata, F. Mizukami, T. Ohta, *Anal. Sci.* **1999**, *15*, 107.
[116] S. Iwai, T. Kamata, S. Murata, K. Yamamoto, T. Ohta, *J. Lumin.* **2000**, *87–89*, 629.
[117] K. Yamamoto, T. Kamata, S. Iwai, S. Kazaoui, N. Minami, F. Mizukami, K. Misawa, T. Ohta, T. Kobayashi, *Chem. Phys. Lett.* **1999**, *302*, 609.
[118] S. Iwai, T. Kamata, K. Yamamoto, T. Fukaya, S. Murata, F. Mizukami, T. Ohta, M. Tachiya, *J. Lumin.* **1998**, *76–77*, 226.
[119] H. Yersin, G. Gliemann, U. Rössler, *Solid State Commun.* **1977**, *21*, 915.
[120] T. Kamata, T. Fukaya, H. Matsuda, F. Mizukami, M. Tachiya, R. Ishikawa, T. Uchida, *J. Phys. Chem.* **1995**, *99*, 13239.
[121] T. Kamata, T. Fukaya, T. Kodzasa, H. Matsuda, F. Mizukami, *Mol. Cryst. Liq. Cryst.* **1995**, *267*, 117.
[122] T. Kamata, T. Kodzasa, H. Ushijima, *Colloids Surf. A* **2002**, *198–200*, 339.
[123] K. Yamamoto, T. Kamata, Y. Yoshida, K. Yase, T. Fukaya, F. Mizukami, T. Ohta, *Chem. Mater.* **1998**, *10*, 1343.
[124] T. Kamata, T. Kodzasa, H. Ushijima, K. Yamamoto, T. Ohta, S. Roth, *Chem. Mater.* **2000**, *12*, 940.
[125] S. Isoda, M. Tsujimoto, K. Yoshida, T. Kobayashi, T. Kamata, *Mol. Cryst. Liq. Cryst.* **1998**, *316*, 15.
[126] J. S. Miller, S. Z. Goldberg, *Inorg. Chem.* **1975**, *14*, 2294.

[127] T. Tano, T. Kodzasa, H. Ushijima, T. Kamata, *Mol. Cryst. Liq. Cryst.* **2000**, *349*, 315.
[128] I. Shirotani, J. Hayashi, K. Takeda, *Mol. Cryst. Liq. Cryst.* **2005**, *442*, 157.
[129] K. Yabuuchi, D. Kawamura, M. Inokuchi, I. Shirotani, J. Hayashi, K. Yakushi, H. Kawamura, H. Inokuchi, *Mol. Cryst. Liq. Cryst.* **2006**, *455*, 81.
[130] M. Inokuchi, D. Kawamura, Y. Sakka, K. Yabuuchi, K. Yakushi, I. Shirotani, J. Hayashi, H. Kawamura, H. Inokuchi, *J. Low Temp. Phys.* **2006**, *142*, 211.
[131] K. Takeda, I. Shirotani, K. Yakushi, *Chem. Mater.* **2000**, *12*, 912.
[132] K. Ohta, M. Ikejima, M. Moriya, H. Hasebe, I. Yamamoto, *J. Mater. Chem.* **1998**, *8*, 1971.
[133] T. Kamata, S. Curran, S. Roth, T. Fukaya, H. Matsuda, F. Mizukami, *Synth. Met.* **1996**, *83*, 267.
[134] A. G. Sharpe, D. B. Wakefield, *J. Chem. Soc.* **1957**, 281.
[135] M. Mégnamisi-Bélomeé, *J. Solid State Chem.* **1979**, *27*, 389.
[136] K. Yoshida, S. Isoda, T. Nemoto, T. Kobayashi, N. Sato, I. Shirotani, *Mol. Cryst. Liq. Cryst.* **2000**, *342*, 121.
[137] M. Megnamisi-Belombe, *J. Solid State Chem.* **1977**, *22*, 151.
[138] H. Ozaki, M. Suhara, M. Taki, K. Akaike, O. Endo, K. Takeda, I. Shirotani, *J. Electron Spectrosc. Relat. Phenom.* **2007**, *156–158*, 351.
[139] I. Shirotani, N. Minobe, Y. Ohtsuki, H. Yamochi, G. Saito, *Chem. Phys. Lett.* **1988**, *147*, 231.
[140] T. Yaji, K. Yoshida, M. Tsujimoto, T. Nemoto, H. Kurata, S. Isoda, *Mol. Cryst. Liq. Cryst.* **2007**, *463*, 293.
[141] T. Yaji, K. Yoshida, S. Isoda, T. Kobayashi, N. Sato, I. Shirotani, *Thin Solid Films* **2001**, *393*, 319.
[142] I. Shirotani, K. Takeda, F. Onuma, N. Sato, *Mol. Cryst. Liq. Cryst.* **1996**, *285*, 119.
[143] K. Takeda, I. Shirotani, J. Hayashi, H. Fukuda, K. Ito, *Mol. Cryst. Liq. Cryst.* **2006**, *452*, 113.
[144] K. Takeda, I. Shirotani, K. Yakushi, *Synth. Met.* **2003**, *133–134*, 415.
[145] K.-i. Sakai, T. Hasegawa, M. Ichikawa, Y. Taniguchi, *Chem. Lett.* **2006**, *35*, 302.
[146] J. W. Menter, *Proc. R. Soc. London, Ser. A* **1956**, *236*, 119.
[147] F. P. Bowden, L. T. Chadderton, *New Scientist* **1962**, *12*, 559.
[148] R. J. C. Brown, A. R. Kucernak, A. G. Taylor, *Thin Solid Films* **2005**, *476*, 373.
[149] M. Ashida, N. Uyeda, E. Suito, *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2616.
[150] C. J. Brown, *J. Chem. Soc. A* **1968**, 2494.
[151] A. L. Balch, R. H. Holm, *J. Am. Chem. Soc.* **1966**, *88*, 5201.
[152] L. F. Warren, *Inorg. Chem.* **1977**, *16*, 2814.
[153] I. L. Eremenko, S. E. Nefedov, A. A. Sidorov, M. O. Ponina, P. V. Danilov, T. A. Stromnova, I. P. Stolarov, S. B. Katser, S. T. Orlova, M. N. Vargaftik, I. I. Moiseev, Y. A. Ustynyuk, *J. Organomet. Chem.* **1998**, *551*, 171.
[154] S. Sato, M. Haruki, S. Kurita, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1990**, *46*, 1107.
[155] R. Palmans, D. B. MacQueen, C. G. Pierpont, A. J. Frank, *J. Am. Chem. Soc.* **1996**, *118*, 12647.
[156] J. R. Hall, R. A. Plowman, *Aust. J. Chem.* **1956**, *9*, 143.
[157] D. R. Lide, *CRC Handbook of chemistry and physics*, 84th ed., CRC Press, Boca Raton, **2003**.
[158] A. Souchay, E. Lenfsen, *Ann. Chem. Pharm.* **1858**, *105*, 245.
[159] G. C. Stevens, *Platinum Met. Rev.* **1979**, *23*, 23.
[160] A. E. Underhill, D. M. Watkins, *Chem. Soc. Rev.* **1980**, *9*, 429.
[161] A. E. Underhill, *Philos. Trans. R. Soc. London, Ser. A* **1985**, *314*, 125.
[162] A. Braude, K. Carneiro, C. S. Jacobsen, K. Mortensen, D. J. Turner, A. E. Underhill, *Phys. Rev. B: Condens. Matter* **1987**, *35*, 7835.
[163] M. Mizuno, A. E. Underhill, K. Carneiro, *J. Chem. Soc., Dalton Trans.* **1983**, 1771.
[164] A. E. Underhill, M. Mizuno, K. Krogmann, M. Rosch, *J. Phys.* **1983**, *44*, 1331.
[165] Y. Sakamoto, G.-e. Matsubayashi, T. Tanaka, *Inorg. Chim. Acta* **1986**, *113*, 137.
[166] S. K. Hurst, L. Spangler, E. H. Abbott, R. Larsen, E. S. Peterson, *Inorg. Chim. Acta* **2005**, *358*, 173.
[167] K. Krogmann, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 35.
[168] M. Mizuno, *Synth. Met.* **1986**, *16*, 199.
[169] M. Mizuno, *Synth. Met.* **1987**, *19*, 963.
[170] K. H. Lee, J. H. Kim, M. Mizuno, *Bull. Korean Chem. Soc.* **1987**, *8*, 137.
[171] A. E. Underhill, M. Mizuno, D. M. Watkins, *Mol. Cryst. Liq. Cryst.* **1982**, *81*, 217.
[172] K. Sakai, N. Akiyama, M. Mizota, K. Yokokawa, Y. Yokoyama, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, m408.
[173] B. M. Anderson, S. K. Hurst, L. Spangler, E. H. Abbott, P. Martellaro, P. J. Pinhero, E. S. Peterson, *J. Mater. Sci.* **2006**, *41*, 4251.
[174] O. Bekaroglu, M. El Sharif, H. Endres, H. J. Keller, *Acta Crystallogr., Sect. B: Struct. Sci.* **1976**, *32*, 2983.
[175] G.-Q. Wu, W.-Z. Chen, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, m1144.
[176] C. Yamamoto, H. Nishikawa, M. Nihei, T. Shiga, M. Hedo, Y. Uwatoko, H. Sawa, H. Kitagawa, Y. Taguchi, Y. Iwasa, H. Oshio, *Inorg. Chem.* **2006**, *45*, 10270.
[177] H. Toftlund, *Chem. Scr.* **1981**, *17*, 196.
[178] B. J. Keller, S. K. Hurst, S. O. Dunham, L. Spangler, E. H. Abbott, E. S. Peterson, *Inorg. Chim. Acta* **2004**, *357*, 853.
[179] K. Sakai, N. Akiyama, M. Mizota, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2003**, *59*, m636.
[180] K. Nayak, D. Bhaumik, J. E. Mark, *Synth. Met.* **1986**, *14*, 309.
[181] L. Xu, S. J. Dong, *J. Chem. Soc., Chem. Commun.* **1994**, 1109.
[182] L. Xu, F. L. Li, S. J. Dong, *Electroanalysis* **1995**, *7*, 734.
[183] L. Xu, S. J. Dong, *Electrochim. Acta* **1994**, *39*, 2599.
[184] B. M. Anderson, S. K. Hurst, L. Spangler, E. H. Abbott, **2009**, article to be published.
[185] K. Torigoe, Y. Nakajima, K. Esumi, *J. Phys. Chem.* **1993**, *97*, 8304.
[186] H. Toftlund, *J. Chem. Soc., Chem. Commun.* **1979**, 837.
[187] O. Simonsen, H. Toftlund, *Inorg. Chem.* **1981**, *20*, 4044.
[188] H. Toftlund, personal communication, **2008**.
[189] K. Carnierno, in: *New Horizons of Quantum Chemistry: Proceedings of the Fourth International Congress of Quantum Chemistry* (Eds.: P. O. Löwdin, B. Pullman), Springer, Boston, **1982**, p. 379.
[190] S. O. Dunham, R. D. Larsen, E. H. Abbott, *Inorg. Chem.* **1991**, *30*, 4328.
[191] S. Onuma, K. Horioka, H. Inoue, S. Shibata, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2679.
[192] M. Katoh, K. Miki, Y. Kai, N. Tanaka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1981**, *54*, 611.
[193] N. Y. Kozitsyna, A. E. Gekhman, S. E. Nefedov, M. N. Vargaftik, I. I. Moiseev, *Inorg. Chem. Commun.* **2007**, *10*, 956.
[194] G. Steyl, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2005**, *61*, m1860.

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