Interest in platinum-chain complexes arose from their unusual oxidation states and physical properties. Despite their compositional diversity, isolation of crystalline chains has remained challenging. Here we report a simple crystallization technique that yields a series of dimer-based 1D platinum chains. The colour of the Pt$^{2+}$ compounds can be switched between yellow, orange and blue. Spontaneous oxidation in air is used to form black Pt$^{2.33+}$ needles. The loss of one electron per double salt results in a metallic d$_z^2$ state, as supported by quantum chemical calculations, and displays conductivity of 11 S cm$^{-1}$ at room temperature. This behaviour may open up a new avenue for controllable platinum chemistry.
In 1828, Magnus\textsuperscript{1} reported a one-dimensional (1D) Pt-chain compound that featured alternating \([\text{PtCl}_4]^{2-}\) and \([\text{Pt(NH}_3)_4]^{2+}\) building blocks (\(d_{Pt-Pt} = 3.25\) Å). Magnus' green salt. However, it was not until the turn of the twentieth century that in-depth studies into the structure and reactivity of similar organometallic Pt chains began\textsuperscript{2}. In 1908, the first Pt\textsuperscript{3+} containing compound was discovered through the treatment of cis-PtCl\(_2\)(acetonitrile) with a silver salt (for example, Ag\textsubscript{2}SO\(_4\))\textsuperscript{3}. The material was described as 'platinblau' (platinum blue) because of its characteristic dark blue colour and indirect evidence suggested a polymeric/oligomeric structure involving Pt–Pt interactions\textsuperscript{4,5}. Yet, despite the intriguing colour and nearly a century of enthusiastic efforts by chemists following the discovery, both the crystal and electronic structures of platinblau remain an enigma.

In the late 1960s, a series of conductive (0.1 S cm\(^{-1}\)) 1D Pt chains composed of either \([\text{Pt(CN)}_4]^{2-}\) or \([\text{Pt}((\text{ox})_2)]^{2-}\) (ox = oxalate; Fig. 1) were developed by Krogmann\textsuperscript{6}. The properties of these materials were eventually realized to be a product of partial removal of electrons from the 1D Pt chain\textsuperscript{7}. For the tetranuclear Pt-chain compounds (considered as partial structures of Krogmann’s salts), the one-electron oxidized species (that is, \(\text{Pt}^{2.25+}\)) resulted in a blue compound reminiscent of the platinblau; other Pt-chain compounds with different nuclearity and oxidation states were also observed\textsuperscript{8–12}. Then in 2006, Brédas and colleagues\textsuperscript{13} revisited Magnus' green salt (\([\text{Pt}((\text{NH}_3)_4][\text{PtCl}_4]\)) and showed that the material possesses interesting band properties for conductive applications, owing to the Pt–Pt interactions; later, Drew et al\textsuperscript{14} harnessed similarly highly coloured Pt-chain complexes as selective photonrich sensors.

In a Pt\textsuperscript{2+} chain complex, the highest occupied state is constructed by an alternating array of antibonding Pt d\(_z^2\) orbitals. Oxidation can result in either delocalization of the missing electron over many sites (Pt\textsuperscript{2+ + d}+) 15,16 or formal oxidation from Pt\textsuperscript{2+} \(\rightarrow\) Pt\textsuperscript{3+} (ref. 17). In the past half century, a variety of highly coloured platinum complexes\textsuperscript{18} have been isolated including red\textsuperscript{19}, orange\textsuperscript{20}, yellow\textsuperscript{21,22}, green\textsuperscript{23,24} and blue\textsuperscript{25} Pt-chain materials. In the case of tetranuclear platinum complexes, these colours arise from a variety of oxidation states including Pt\textsuperscript{2+} (Pt(II)\textsubscript{4}), Pt\textsuperscript{2.25+} (Pt(II)\textsubscript{4}Pt(III)\textsubscript{2}), Pt\textsuperscript{2.5+} (Pt(II)\textsubscript{2}Pt(III)\textsubscript{4}) and Pt\textsuperscript{3+} (Pt(III)\textsubscript{4}), although the fully oxidized systems tend to behave as Pt\textsuperscript{3+} dimers with two axial donors.

Around the same time as Krogmann’s developments, Pt\textsuperscript{2+} complexes found application in medicinal chemistry, propelled by the anticancer treatment cis-platin\textsuperscript{26–28}. These works provided an interesting avenue for cis-platin\textsuperscript{26–28} and subsequent focus shifted away from the unusual electronic properties associated with Pt-chain complexes towards molecular reactivity, with complexes often featuring relatively simple ligands similar to those shown in Fig. 2. However, fundamental research into ligand design continued alongside this more applied chemistry.

The amidate ligand (Fig. 1) is interesting, because it produces doubly bridged dimeric Pt\textsuperscript{2+} building blocks. A typical formula is \([\text{Pt}((\text{NH}_3)_4]_2(\mu\text{-amidate})]^{2+}\) (amidate can also be \(\mu\text{-pyridonate, \(\mu\text{-pyridolonate, \(1\text{-methyluracilate, \(1\text{-methylthyminate, acetamidinate and so on}])}\textsuperscript{9–12}. Tetranuclear complexes arise from a stack of two dimeric units where the dimer–dimer interaction is stabilized by ligand-mediated quadruple hydrogen bonds formed between the O(amidate) and N–(amine) units. In such cases, the coordination manner of two amidates must be in a head-to-head (HH) arrangement, permitting a stack of \(\text{N}_2\text{O}_2\)-ligated Pt coordination planes. Moreover, the Pt–Pt bonding interactions within the tetranuclear units are reinforced by shortening the Pt–Pt distances as the oxidation state increases. Both the tetranuclear and octanuclear species exhibit the characteristic partial oxidation associated with the colourful Pt-chain complexes\textsuperscript{29,30}.

With the recent progress in conductive metal-organic framework chemistry\textsuperscript{31–36}, interest in highly conductive hybrid materials has been reignited. Metal-organic materials typically do not have high intrinsic electrical conductivity, because the metals are spatially separated by organic ligands\textsuperscript{37}. These 1D Pt chains pose interesting pathways to access highly ordered and conductive metal-organic wires\textsuperscript{38}. There has only been one dimer-based conductive 1D Pt family\textsuperscript{39}. The material was electrochemically grown in oxidizing conditions and produced a black Pt-chain complex \([\text{Pt}((\text{NH}_3)_4]_2(\mu\text{-acetate})]^{2+}\) that, similar to Krogmann’s Pt salts, was susceptible to partial oxidation at the metal centres. This material demonstrated a moderate electrical conductivity of 0.001–0.01 S cm\(^{-1}\), despite its relatively poor crystallinity.

Here we report the formation of a series of Pt\textsuperscript{2+} Magnus-type double salts: 1D Pt\textsuperscript{2+} chain composed of alternating cationic (\(+\)\(+/–\)) and anionic (2–) Pt\textsuperscript{2+} building blocks. Our initial target was a stoichiometric mixture of \([\text{HT-Pt}((\text{bpy})_2]_2(\mu\text{-pivalamidate})]^{2+}\) (HT indicates a head-to-tail arrangement of the pivalamidate ligands) and \([\text{Pt}((\text{ox})_2]_2(\mu\text{-pivalamidate})]^{2+}\) (1; HT indicates a head-to-tail arrangement of the pivalamidate ligands and \([\text{Pt}((\text{ox})_2]_2(\mu\text{-pivalamidate})]^{2+}\) (2); however, the result is a new family of compounds. We detail the crystallization procedure, followed by characterization of their crystal structure and physical properties including colour and electrical conductivity.

**Results**

Crystal growth and characterization. We developed a simple kinetically controlled crystallization procedure to provide access to hitherto unknown Pt-chain systems. The petri-paper three-zone crystallization method (Fig. 2) isolates the reagents, located in zones 1 and 3, from the crystallization region, zone 2. In practice, this is achieved by using filter paper separating the zones, thereby slowing the rate of salt diffusion. Aqueous 1 and 2 were added to zones 1 and 3, respectively. After 2 days, bright yellow crystals of \([\text{HT-Pt}((\text{bpy})_2]_2(\mu\text{-pivalamidate})]([\text{Pt}((\text{ox})_2]_2(\mu\text{-pivalamidate})]^{2+}\) (Supplementary Fig. 1), the yellow crystalline material 3 undergoes the HT\(\rightarrow\)HH isomerization over 24 h through the gradual dissolution of 3 to form the compositionally identical 4.

**Figure 1** | Ligands commonly employed in Pt-chain chemistry: Examples of familiar neutral and anionic ligands found in Pt-chain complexes. The bridging amidate ligand, shown in red, can form hydrogen bonds in the direction of the Pt chain, stabilizing the Pt centres and promoting oxidation.

Neutral
---
\(\text{NH}_3\)
\(\text{N}\)

Anionic
---
\(\text{O}^-\)
\(\text{CN}^-\)

Head-to-head \(\rightarrow\) Head-to-tail isomerization
\(\text{HN} \rightarrow\) O\(\rightarrow\) O\(\rightarrow\) HN

As observed for the monomeric 1 (that is, the diplatinum cation \([\text{HT-Pt}((\text{bpy})_2]_2(\mu\text{-pivalamidate})]^{2+}\) (Supplementary Fig. 1), the yellow crystalline material 3 undergoes the HT\(\rightarrow\)HH isomerization over 24 h through the gradual dissolution of 3 to form the compositionally identical 4.
([HH-Pt(II)\textsubscript{2}(bpy)\textsubscript{2}(\mu-\text{pivalamidate})\textsubscript{2}][Pt(II)(ox)\textsubscript{2}] \cdot 5.5\text{H}_2\text{O}) \text{ (bright orange needles shown in Fig. 3b). Relative to 3, the pivalamidate-bridged Pt–Pt distances decrease by } \sim 0.1 \text{ Å, which is consistent with the preference of HT-Pt(II)\textsubscript{2} dimers for a bridged Pt–Pt distance longer than the corresponding HH-Pt(II)\textsubscript{2} dimers, probably due to higher electrostatic repulsion given within a symmetric dimeric structure having two N\textsubscript{3}O-ligated Pt geometries\textsuperscript{24}.}

Remembering that the highest occupied states of Pt\textsuperscript{2+}-chain complexes are $\sigma^*(d_{z^2} - d_{x^2-y^2})\textsuperscript{11}$, the colours associated with Pt compounds are principally correlated with the lowest-energy optical transition, corresponding to the so-called metal-metal-to-ligand charge transfer transition. Compound 4 has shorter Pt–Pt bonds, leading to greater destabilization of the $\sigma^*$, and hence to the red shift in transition energy. In addition, the adjacent bipyridine ligands interact, lowering the lowest unoccupied molecular orbital energy proportional to inter-Pt distance (resulting in a red shift with HT $\rightarrow$ HH isomerization).

During the pivalamidate HT $\rightarrow$ HH isomerization and subsequent crystallization of 4, a structurally dissimilar blue
Figure 4 | Electronic properties of compound 6. [HT-Pt$_2$(bpy)$_2$(µ-pivalamidate)$_2$][Pt(ox)$_2$(NO$_3$)$_2$]·7H$_2$O, 6, where the calculated spin density (blue isosurface at 0.02 e/Å$^3$) is delocalized along the Pt chain in the <001> direction. The hydration layer solvates (NO$_3$)$_2$ in [200], shown as purple plane (a). The electronic band structure (b) depicts the metallic character in the direction of the delocalized Pt$^{2.33+}$ chain. The addition of 2e$^-$ (denoted by *) increases the Fermi level (dotted line) to fill the valence band, resulting in a semiconducting band gap analogous to 3. The target synthesis of 6 resulted in large black needles (c), which could be mounted directly for conductivity measurements (d). Using gold paste contacts provided a peak conductivity of 11 S cm$^{-1}$, whereas the carbon paste used in the temperature sweeping measurement (e) produced a peak conductivity of 2.2 S cm$^{-1}$ at $\sim$210 K. O, H, N, C and Pt are depicted in red, white, blue, black and grey, respectively.

Discussion

Unlike the colourful Pt-chain complexes, black compounds are interesting for electronic applications, owing to their potentially high conductivity and strong optical absorption. Before this, there has only been one Pt-black chain complex reported$^{39}$. Quantum chemical calculations were used to elucidate the electronic structure of 6. The unpaired valence electrons are delocalized along the Pt chain (Fig. 4a) in agreement with its diamagnetic character evidenced by electron spin resonance spectroscopy. Furthermore, the homogeneous charge distribution about the Pt nuclei is in agreement with X-ray photoemission spectroscopy measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5). From the electronic band structure measurements (Supplementary Figs 10 and 11d, and Supplementary Table 5).
Our study has provided several advances in the synthetic chemistry and property control of Pt salts. First, we demonstrated that controlled crystallization using the petri-paper procedure provides a cheap and accessible method for the recovery of novel structures. Identification of a blue Pt\(^{2+}\) compound suggests that the elusive platinblau may not require non-integral oxidation states. We further showed that oxidation of this double salt to Pt\(^{2+}\) results in a black highly conductive material, as supported by ab initio calculations that revealed a metallic state with delocalized electrons at the Fermi level. This provides an important design principle for developing conductive metal-organic networks, where redox reactions can be used to install conductivity post-synthetically. Our results highlight several important questions including whether we can harness the Pt\(^{2+}\) oxidation for catalysis and whether these double salts can provide an alternative to molecular analogues for Pt\(^{2+}\)-based medicines? We anticipate that these findings will stimulate further interest in fundamental platinum chemistry.

**Methods**

**Synthetic approach.** [HT-Pt(II)(bpy)]\(2\)(μ-pivalamidate)\(_3\)\([NO_3]_2\), 5H_2O, 1, was prepared as previously described by Yokokawa and Sakai\(^{28}\), and K\(_2\)[Pt(ox)\(_2\)\]·2H_2O, 2, was prepared as previously described by Werner and Grebe\(^{2}\). Using the petri-paper three-dimensional aqueous solution 1 and 2 were added to zones 1 and 3, respectively. The crystals were then developed (that is, in air), at room temperature, within a few days, sequentially crystallizing as [HT-Pt(II)(bpy)]\(2\)(μ-pivalamidate)\(_3\)\([NO_3]_2\), 3 (yellow needles), [HT-Pt(II)(bpy)]\(2\)(μ-pivalamidate)\(_3\)\([NO_3]_2\), 5.5H_2O, 4 (orange needles) and [HT-Pt(II)(bpy)]\(2\)(μ-pivalamidate)\(_3\)\([NO_3]_2\), 8.5H_2O, 5 (dark blue plates, hexaplannum species). Representative crystals were removed from the reaction mixture and physical property measurements were performed on them. Leaving of the mixture for 1–2 weeks led to the formation of [HT-Pt(II)(bpy)]\(2\)(μ-pivalamidate)\(_3\)\([NO_3]_2\), 7·H_2O, 6 (fine black needles), a partially oxidized species. Although this sequential procedure resulted in very low yields, a refined target synthesis involving permanganate improved synthetic yields to ca. 21% (see Supporting information). Oxidation by persulfate, (ii) ageing of crystals at higher temperature and (iii) manual oxidation by persulfate, (ii) ageing of crystals at higher temperature and (iii) manual

**Computational approach.** All calculations were performed within the Kohn–Sham density functional theory framework using periodic boundary conditions, to approximate the infinite salts, starting from the crystallographic unit cells determined from the XRD measurements. The Vienna ab initio simulation package\(^{24}\), a plane-wave code (with PAW scalar relativistic core potentials)\(^{35}\), was employed for all geometry optimizations and electronic calculations. For each system, the lattice vectors and internal atomic positions were relaxed with the semi-local Perdew–Burke–Ernzerhof exchange-correlation functional revised for solids\(^{46}\). For these calculations, a 500-eV plane-wave cutoff basis set was found to be suitable for convergence of the systems to within 0.01 eV per atom. To provide quantitative electronic information, non-local hybrid density functional theory calculations were performed using the HSE06 functional\(^{47}\), with 25% of the short-range semi-local exchange functional replaced by the exact non-local Hartree–Fock exchange. Visualizations of the structures and orbitals were made using the codes VESTA\(^{48}\).

**Data availability.** The input structures for the solid-state quantum mechanical calculations are available from https://github.com/WMD-group/Crystal_structures. The X-ray crystallographic coordinates for structures reported in this study have been deposited at the Cambridge Crystallographic Data Centre (CCDC), under deposit numbers CCDC 1477434–1477437. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Author contributions
All compounds were prepared by Y.K. and K.S. The petri-paper method was invented by Y.K. and K.S. Improved synthesis of compound 6 was developed by N.A. T.I., T.K. and K.S. performed the crystallographic measurements and structure refinement. Electrical conductivity measurements were carried out by N.A., K.S. and H.K. C.H.H. and A.W. performed the density functional theory calculations. C.H.H., A.W. and K.S. wrote the paper.

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