Chain Compounds Based on Transition Metal Backbones: New Life for an Old Topic

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1. Interest in One-Dimensional Materials

One-dimensional and "pseudo" one-dimensional materials have long fascinated physicists and chemists because of their unusual properties but, over the last two decades, research activity in this area had been steadily declining. One possible explanation for this trend is that researchers have been preoccupied with the search for materials that exhibit high-temperature superconductivity and magnetic ordering, properties that are not typically associated with one-dimensional (1D) materials. As with many trends in science, however, this situation has now come full circle. Research in the preparation and characterization of materials with high anisotropy and restricted dimensionality is currently paving the way for a new era of nanoscale science and technology. The reason for this is very simple: tiny pieces of matter exhibit very unusual optical, magnetic, and conducting properties due to their size. Much of the current attention in nanoscience is being directed at the study of small domains in the form of quantum dots, nanotubes, and electrically or magnetically bistable molecules.

Decades before the term "molecular wire" came into common usage, physicists and chemists recognized that mixed-valence stacks of organic as well as inorganic molecules exhibit unusual electrical properties. The general goal of this area was to prepare "synthetic metals", but the possibility of stabilizing the superconducting state in low-dimensional materials was also contemplated. This interest was largely fueled by the exciton theory of superconductivity proposed by W. A. Little in 1964,[1] and by the report of superconducting fluctuations in the 1D metal [(TTF)(TCNQ)] by Heeger and co-workers in 1973.[2] Little's theory, which is based on an electron-polarization (exciton) coupling mechanism, predicts that a superconducting material with a T_c value as high as room temperature is possible in 1D systems composed of a conducting backbone and photochemically active side-chains (dye molecules). The theory was never actually tested, however, because of the lack of an appropriate chemical system, and it gradually faded into obscurity.[3] A recent report has led to renewed speculation about Little's exciton theory of superconductivity and about the properties of 1D polymeric materials in general.[4]

During the decades spanning the period 1960–80, a considerable body of literature was published on the synthesis and properties of materials composed of interacting metal ions along the backbone of a chain.[5] One of the largest classes of these materials is the family of partially oxidized tetracyanoplatinate salts, commonly referred to as Krogmann salts.[6] The square-planar $[Pt(CN)_4]^{n-}$ anions in these materials form infinite stacks in the solid state based on the overlap of the d_{z^2} orbitals normal to the plane of the molecule. The short Pt···Pt contacts lead to band formation (Figure 1), and oxidative doping of the Pt^{II} compounds produces nonstoichiometric conducting phases. For example, salts of the type

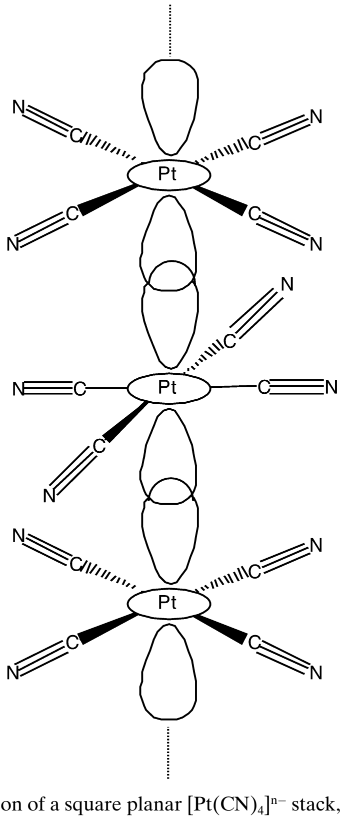

Figure 1. A schematic representation of a square planar $[Pt(CN)_4]^{n-}$ stack, to emphasize the overlapping d_{z^2} orbitals.

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$K_2[Pt(CN)_4]X_{0.3}\cdot(H_2O)_n$ (X = Cl, Br) in which platinum has an average oxidation state of approximately +2.3, exhibit metallic luster and high conductivity. These materials represent the first synthetically designed "wires" based on inorganic molecules. It is worth noting that, in recent years, a new family of Pt chains based on alternating cations and anions of the types $[Pt(CNR)_4]^{2+}$ (R = *i*Pr, *c*-$C_{12}H_{23}$, *p*-$(C_2H_5)C_6H_4$) and $[Pt(CN)_4]^{2-}$ has been reported. These are being explored as novel vapochromic sensor materials.[7]

2. Renaissance of 1D Metal–Metal Chain Compounds

The subject of this Highlight article is the recent renaissance of research in the area of 1D oligomers and polymers with metal-containing backbones. There is a systematic effort currently underway in a number of laboratories to design and understand the properties of compounds based on linear chains of transition-metal atoms. The new research is divided into two distinct types of activities. In one approach, the metal atoms are positioned in a linear array by the use of carefully designed ligands. In this manner, researchers have demonstrated that they can prepare oligomers composed of a predetermined number of metal ions. In a completely different approach, it has been shown that it is possible to use stable, dinuclear metal–metal bonded precursors as building blocks for polymeric chains.

3. Oligomers based on M–M Interactions Engendered by Polydentate Ligands

3.1. Polypyridylamine Ligands

One method for stabilizing M_n^{m+} chains is to bring the metal ions into close proximity by the use of specifically designed polydentate ligands whose number and orientation of donor atoms determines the nuclearity of the product. The use of polypyridylamine ligands with flexible backbones is a particularly attractive choice that has led to the isolation of metal chains with 3–9 metal atoms. By employing this approach, the independent research groups of Cotton and Peng have prepared a family of trinuclear compounds of the type $[M_3(\mu_3\text{-dpa})_4X_2]$ (M = Cu,[8a] Ni,[8b] Cr,[8c] Ru,[8d] Rh,[8d] Co;[8e–g] dpa = *syn-syn* bis(α-pyridyl)amido; Figure 2). Interestingly, the tricobalt analogues exhibit fascinating subtleties in their molecular structures in that both the symmetrical (s; Co–Co distance 2.3178(9) Å)[8g] and unsymmetrical (u; Co–Co distances 2.294(1) and 2.466(1) Å) analogues can be isolated.[9] These observations have led to renewed speculation of the possibility of the existence of "bond stretch isomers". As discussed in detail in the recent literature,[10] all previous claims of bond stretch isomerism can be attributed to crystallographic artifacts. In the case of the s- and u-$[Co_3(dpa)_4Cl_2]$ compounds, however, there is no question about the chemical formula and there are no problems resulting from disorder. Whether this molecule represents a true case of bond stretch isomerism or not is unclear, however, the fact that both a symmetrical trinuclear chain and a dinuclear Co–Co unit with an independent Co^{II} "appendage" can be stabilized in the solid state, represents an intriguing example of how crystallization conditions can have a profound effect on the structural parameters of a simple molecule.[9] Apart from this intriguing issue, the magnetic properties of the tricobalt compounds are also quite interesting, as they show spin-crossover behavior that varies with the nature of the solid-state structure.[11]

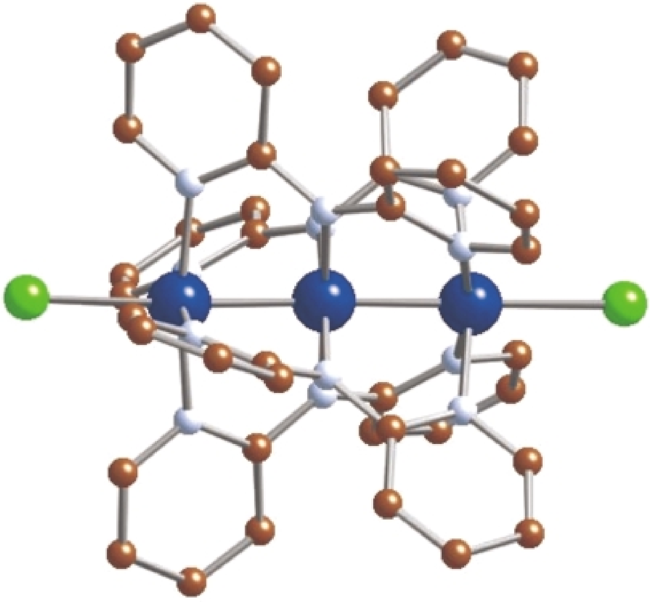

Figure 2. Molecular structure of the tricobalt molecule, $[Co_3(\mu_3\text{-dpa})_4Cl_2]$ (dpa = *syn-syn* bis(α-pyridyl)amido).

The success of the aforementioned approach has progressed well beyond the preparation of trinuclear compounds. Indeed, by sequentially adding binding sites to the ligands, it is possible to prepare higher nuclearity analogues, for example, M_5 linear chains (M = Ni,[12a,b] Cr;[12c,d] ligand: *N*,*N'*-bis(α-pyridyl)-2,6-diaminopyridine or tripyridyldiamine (H_2tpda)), M_7 chains (M = Ni,[13a] Cr;[13b] ligand: tetrapyridyltriamine (H_3teptra); Figure 3) and M_9 chains (M = Ni;[13c] ligand: pentapyridyltetramine (H_4peptea).

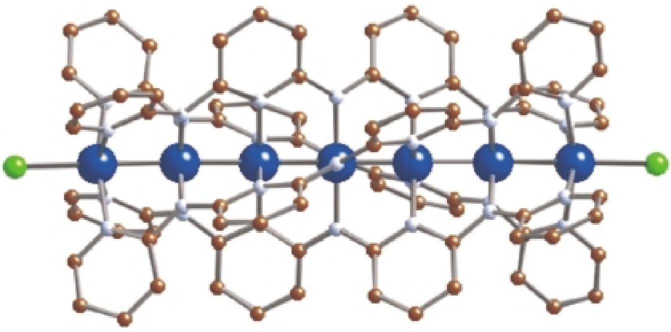

Figure 3. Molecular structure of the heptanickel molecule, $[Ni_7(\mu_7\text{-teptra})_4Cl_2]$ (teptra = tetrapyridyltriamino).

3.2. Olefin Ligands

One recent finding that is particularly interesting in the context of 1D metal "wires" is the report that unsaturated hyrdocarbons can be used as to construct Pd chains surrounded by a "π-electron sheath".[14] The groups of Murahashi and Kurosawa reported that mononuclear Pd^0 and Pd^{II} precursors react with conjugated polyenes to form linear Pd–Pd bonded chains stabilized solely by the olefin ligands. The authors have isolated "sandwich chains" with three, four, and five Pd atoms by this approach. A single-crystal X-ray diffraction study of the tetrapalladium molecule confirmed the formulation as a Pd–olefin chain compound whose molecular structure is depicted in Figure 4.[14c]

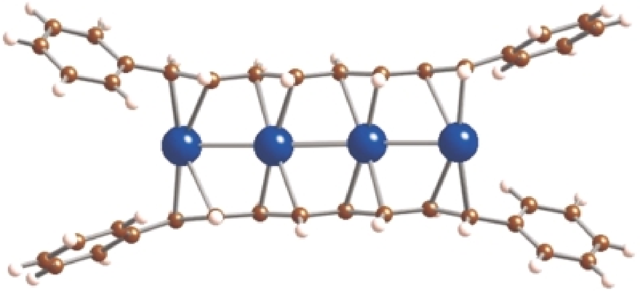

Figure 4. Molecular structure of the tetrapalladium cation, $[Pd_4(DPOT)_2]^{2+}$ (DPOT = *all-trans*-1,8-diphenyl-1,3,5,7-octatetraene).

The Pd–olefin "wires" are of interest for several reasons. They constitute the first examples of metal–metal bonded arrays stabilized entirely by metal–carbon bonds, which constitutes a significant contribution to organometallic chemistry.[15] Most importantly, however, the supporting ligand is a conducting molecule in its own right. The prospect of making more elaborate 1D chains in which a conducting organic and inorganic backbone are embedded in the same architecture is attractive with respect to enhancing conducting behavior, and certainly presents intriguing possibilities for additional work in this area.

3.3. Future Prospects for Ligand-Supported Metal Arrays

One obvious question in the field of ligand-supported metal arrays is how far can one extend the chain length? The main limitation is the maximum number of binding units that can be fused together into one ligand, which is an issue of organic synthesis. In addition to the general challenge of progressively adding binding units to the ligand is the problem of eventual insolubility. If these synthetic barriers can be overcome in the next generation of chains, it may be possible to prepare molecules whose chain lengths approach a size regime that allows for measurements to be made on individual molecules.

4. Oligomers and Polymers Based on Unsupported M–M Interactions

4.1. Oligomeric Mixed-Valence Chains

The $[Rh_4(1,3\text{-diisocyanopropane})_8Cl]^{5+}$ ion, reported by Gray[16a, b] and Mann,[16c] was the first structurally characterized chain based on the Rh^I-Rh^{II}-Rh^{II}-Rh^I unit (Figure 5). Subsequently, numerous examples of oligomeric mixed-valence rhodium complexes have been prepared.[17] In order to favor the formation of these complexes, it is necessary to use sterically undemanding ligands that do not restrict intermolecular interactions along the axial direction, for example, planar chelating ligands such as 9,10-phenanthroquinonediimine.[18] One particular category of these mixed-valence oligomers is the "Platinum Blue" family.[19] The first X-ray structural characterization of the platinum blues was carried out by Lippard and co-workers[20] who established the existence of the mixed-valence tetranuclear platinum compounds based on $[Pt_4(NH_3)_8(C_5H_6NO)_4]^{5+}$ ions. The tetraplatinum chemistry has been extended to even longer chains of metal atoms, for example, the octanuclear chains $[\{Pt_2(NH_3)_4(CH_3CONH)_2\}_4]^{10+}$ and $[\{Pt_2(NH_3)_4(CH_2FCONH)_2\}_4]^{8.66+}$ in which four sets of amidate-bridged Pt_2 "dimers" are held together by $Pt\cdots Pt$ interactions.[19]

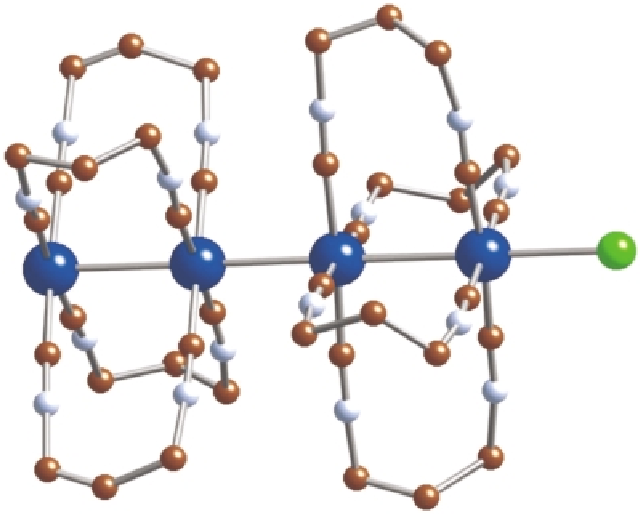

Figure 5. Molecular structure depicting the Rh^I-Rh^{II}-Rh^{II}-Rh^{II}-Cl unit in the $[Rh_4(1,3\text{-diisocyanopropane})_8Cl]^{5+}$ cation.

New developments in this area include the work of Oro and co-workers, who have prepared analogous tetranuclear rhodium and iridium blues.[21] The researchers present two general ways of preparing mixed-valence species of Rh and Ir. The tetrarhodium cation $[Rh(\mu\text{-pz})(CNtBu_2)_4]^{2+}$ (pz = pyrazolato) was obtained by mixing $[\{Rh^I(\mu\text{-pz})(CNtBu)_2\}_2]$ and $[\{Rh^{II}(\mu\text{-pz})(CNtBu)_2(NCCH_3)\}_2][PF_6]_2$ in a 1:1 ratio, and the neutral tetrairidium compound $[\{(NCtBu)_2(I)[Ir^I(\mu\text{-pz})_2\text{-}Ir^{II}(CNtBu)_2]\}_2]$ was prepared by oxidation of $[\{Ir^I(\mu\text{-pz})(CNtBu)_2\}_2]$ with iodine (Figure 6). Both methods appear to be quite general for the preparation of tetranuclear compounds of rhodium and iridium.

4.2. Infinite Mixed-Valence Chains

Discrete dinuclear complexes with metal–metal bonds occupy a central role in modern transition-metal chemistry,[22]

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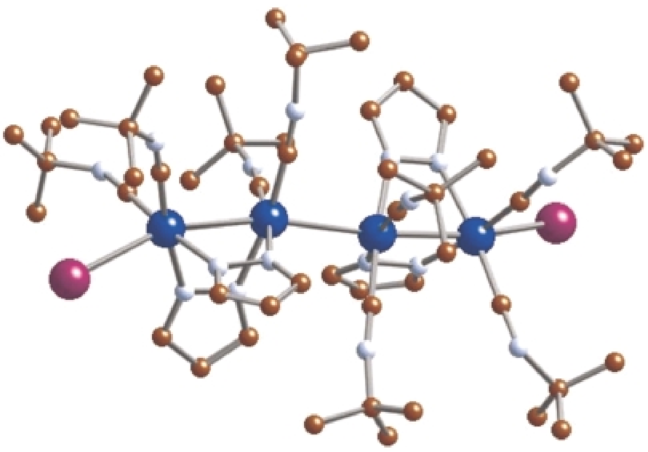

Figure 6. Molecular structure of the tetrairidium molecule, $[\{(\mathrm{CN}t\mathrm{Bu})_2(\mathrm{I})\mathrm{Ir}(\mu\text{-pz})_2\mathrm{Ir}(\mathrm{CN}t\mathrm{Bu})_2\}_2]$.

but it has only been recently demonstrated that these complexes can be used as precursors for 1D metal chains. Infinite metal-based chains are expected to be much more promising as conducting inorganic "molecular wires" than short-chain oligomers. Work in our laboratories in this area has led to the isolation of the novel solvated 1D rhodium chain, $[\{\mathrm{Rh}(\mathrm{CH_3CN})_4\}(\mathrm{BF_4})_{1.5}]_\infty$, obtained by slow reduction of $[\mathrm{Rh_2(CH_3CN)_{10}}][\mathrm{BF_4}]_4$ at a Pt electrode (Figure 7).[23] The infinite chain results from radical polymerization of the unstable mixed-valence $\mathrm{Rh}^{\mathrm{I,II}}_2$ species and consists of alternating Rh–Rh interactions of 2.8442(8) and 2.9277(8) Å. This compound is the first example of an infinite metal-containing chain synthesized from a dimetal precursor, and it provides a rare opportunity to probe 1D behavior in a metal chain that differs considerably from the mixed-valence $[\mathrm{Pt(CN)_4}]^{n-}$ systems. Although the charge transport experiments indicate that $[\{\mathrm{Rh}(\mathrm{CH_3CN})_4\}(\mathrm{BF_4})_{1.5}]_\infty$ is a semiconductor, theoretical calculations predict that the d_{z^2} orbitals interact quite strongly along the chain. It is feasible to expect that a metallic state could be stabilized with subtle chemical modifications.

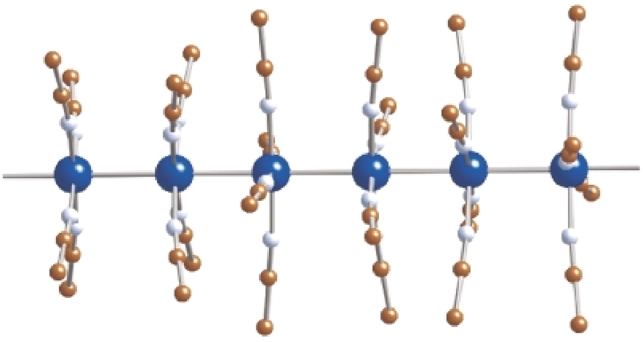

Figure 7. A section of the infinite cationic chain in $[\{\mathrm{Rh}(\mathrm{CH_3CN})_4\}(\mathrm{BF_4})_{1.5}]_\infty$.

It is interesting to note that the prospect for isolating linear chains of interacting dirhodium metal ions is not limited to acetonitrile chemistry. One recent example of such a system is a 1D chain compound composed of the repeat units $[\{\mathrm{Rh}^{\mathrm{II,II}}_2(\mathrm{O_2CCF_3})_4\}\{\mathrm{Rh}^{\mathrm{I,I}}_2(\mathrm{O_2CCF_3})_2(\mathrm{CO})_4\}_2]$.[24] In addition, dirhodium-containing metal chains of the type $[\{\mathrm{Rh_2(O_2CCH_3)_2(bpy)_2}\}(\mathrm{BF_4})\cdot\mathrm{H_2O}]_n$ have been prepared by one-electron reduction reactions of $[\mathrm{Rh_2(O_2CCH_3)_2(bpy)_2(H_2O)_2}]^{2+}$ in alcohols.[25, 26] The X-ray structures of one of these products revealed that intermolecular Rh ⋯ Rh separations are much longer (2.833(2) Å) than the intramolecular interactions (2.666(2) Å), which is an indication of the stabilizing influence of the bridging acetate ligands in the parent complex.

4.3. Future Prospects for Unsupported Metal Chains

The successful isolation of infinite mixed-valence rhodium chains from dinuclear precursors leads to an obvious question, namely, will it be possible to prepare metal chains with other 4d and even 5d metal ions? Possible candidates for this chemistry are $\mathrm{Os}^{\mathrm{II,III}}$ and $\mathrm{Ir}^{\mathrm{I,II}}$ species. The choice of suitable precursors and the optimization of crystal growth conditions are the key issues that need to be explored. The recent explosion of interest in nanoscale electronic devices is expected to fuel the growth of this chemistry and related topics in the coming years.

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[26] We have recently obtained structural characterization of the analogous chloride complex $[\{Rh_2(O_2CCH_3)_2(bpy)_2\}Cl\cdot 3\,CH_3OH]$. K. Sorasaenee, K. R. Dunbar, unpublished results. The presence of the chloride anion in the crystal leads to three sets of Rh–Rh distances, 2.6755(6) (intramolecular), 2.7858(7) and 2.9034(7) Å (both intermolecular).