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NEW HIGHLY CONDUCTING COORDINATION COMPOUNDS.(U)
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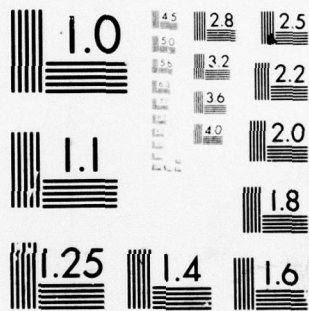
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New Highly Conducting Coordination Compounds

by

D. B. Brown, K. Carneiro, P. Day, B. Hoffman,
H. J. Keller, W. A. Little, A. E. Underhill
and J. M. Williams

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NEW HIGHLY CONDUCTING COORDINATION COMPOUNDS

D.B. Brown, K. Carneiro, P. Day (Recording Secretary),
B. Hoffman, H.J. Keller (Chairman), W.A. Little,
A.E. Underhill and J.M. Williams

I. Introduction

The past 10-15 years have seen an extensive search in many laboratories for coordination complexes which exhibit high conductivity in the solid state. Indeed the chemical systems which have given us properties illuminating most clearly the basic physics of the one dimensional state have been of this type. However, until recently, physical measurements on highly conducting metal coordination compounds have concentrated on the single inorganic prototype one-dimensional (1-D) conductor $K_2Pt(CN)_4 \cdot Br_{0.3} \cdot 3H_2O$, KCP, simply because of a scarcity of other well characterized examples. This unusual situation was, in retrospect, of great benefit. The strikingly unusual properties of KCP and related compounds have been an intellectual attraction, particularly for the physicists and the challenging problems relating to fluctuations, disorder, competing instabilities and broken symmetry have attracted many of the most distinguished solid state scientists to the field. Their contributions, although relatively abstract, have played a key role in building our present understanding of these materials. In addition the field has served to develop a variety of interdisciplinary collaborations, from which each discipline is now benefiting. In particular, because the field has proved challenging to synthetic inorganic chemists, it has been possible to screen the conducting behavior of a sufficiently large number of complexes to allow one to establish some guidelines which may now be summarized.

II. Basic Considerations

A fundamental requirement for high conductivity in any solid material is the attainment of a high intermolecular transfer integral, t , so we begin by pointing out some ways in which that

in any solid transfer in which that

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may be established in coordination complexes. In this type of compounds one normally has a metal ion (M) in a positive oxidation state (+1 to +4), typical ligands (L) being monoatomic (halide or oxide ions), diatomic (CN^-), or conjugated polyatomic from organic isocyanides through bifunctional aromatics such as pyrazine and bipyrimidine up to the very large planar ring systems such as porphyrin and phthalocyanines. Contact between the metal centers in the solid state may come about either by direct overlap or via a bridging group. To maximize the former, one needs planar complexes which can be stacked on top of one another or bridging groups which subtend a sufficiently small MLM -angle. Planar complexes are associated with quite specific d-electron configurations, principally low spin d^8 , unless rigid ligands are employed to force the metal ion into a planar coordination. Direct MM interaction is inherently desirable because the presence of a bridging group at once attenuates the MM transfer integral by the square of the ML overlap integral. Where polyatomic bridging ligands like pyrazine are concerned, intramolecular π - π overlap within the conjugated aromatic system is sufficiently large that electron migration from one end of the bridging molecule to the other is not hindered. In this context lower oxidation states generating greater ML covalency via larger orbital extension might be a desirable goal.

A second requirement for high mobility is to lower both the on-site and inter-site Coulomb repulsion. In the context of metal complexes this is better achieved in partially oxidized "non integral oxidation state" (NIOs) systems than in ones where the electron: atomic ratio is integral (IOS). The NIOs crystals based on coordination compounds which have been studied to date can be broken down into two classes. On the one hand, there are systems, exemplified by the tetracyanoplatinate salts, where the transport properties can almost completely be understood in terms of carriers confined to a conducting spine of metal atoms. The coordinated ligands (eg CN^-), although essential for defining the properties of the parent IOS molecule or ion, play little or no direct part in the charge transport process. On the other hand there are systems, such as the metalloporphyrins and their analogues, in which the carriers are essentially ligand based; the metal ion acts in a decisive manner to modify the ligand properties, but in this case the transport process does not appear to directly involve the metal.

III. Integral Oxidation State Compounds

IOS compounds in which a molecule, or ion, bridges adjacent metal centers have rarely been found to exhibit any appreciable conductivity, although substantial magnetic exchange interactions between partly occupied localized metal orbitals are frequently observed. When the metal atoms are in direct contact too, high conductivity remains the exception when the oxidation state (electron/atom ratio) is integral. Examples are the well known metal atom chain compounds of Ni^{II} , Pt^{II} and Pt^{II} such as the dimethylglyoximates

and tetracyanides which are excellent insulators at ambient pressure though there are indications that they can be rendered conducting if a large (100 kbar) applied pressure is used to bring the metal atoms closer together. On the other hand such compounds do show very unusual optical properties indicative of a substantial MM interaction in their excited states. A further example would be $\text{Ir}(\text{CO})_3\text{Cl}$, now thought to be an IOS compound, though quite a good conductor at ambient pressure.

Turning to 1D compounds in which the electron/atom ratio varies from one metal ion site to the next, but in which the metal ion sites are connected through ligands, trapped valency and localized electron behavior remains the rule. Compounds like $\text{Pt}(\text{NH}_3)_2\text{Cl}_3$ remain insulators at atmospheric pressure though they, too, can be rendered conducting under pressure. We point out, however, that in some discrete dimeric mixed valence metal complexes with bridging groups like pyrazine and N_2 the electrons may be delocalized between the metal atoms in a manner which, if extended to an infinite chain, would lead to formation of an energy band with a finite density of states at the Fermi surface. Further synthetic efforts in this direction would be highly desirable.

IV. Non Integral Oxidation State Complexes, Direct MM Overlap

From the discussion so far it is clear that high conductivity is most likely to be found in NIOS compounds. Three primary variables must be considered in synthesizing materials with directly interacting metal centers: the nature of the IOS precursor, the identity of the oxidant, and the synthetic technique for combining the two. Because of the geometrical constraints, most new highly conducting materials are likely to derive from the oxidation of square-planar d^8 complexes.

Three basic synthetic techniques have been used to generate NIOS materials. The first, involving crystallization from solutions containing both oxidized and reduced forms of the metal complex, has thus far been successful in only a few cases, most notably KCP itself. The second, involving electrochemical oxidation of solutions of the IOS precursor, has been remarkably successful in generating pure single crystals of a variety of KCP analogs, but has not been utilized in many other systems. The third approach, solid state oxidation of appropriately stacked precursors has rarely produced high quality crystals, but has the advantage of providing a range of redox potentials for the oxidant and a variety of geometrical and chemical features which may be incorporated into the resulting structure. At this point, there are not sufficient experimental data available to determine the effects of these variations, and much more experimental effort is required.

Further, the nature of the ligands, which potentially provides the greatest synthetic variability, must be examined in the future

in much more detail. We believe that the following specific features of ligand variation require investigation. First, there may be a relationship between conductivity and such donor atom properties as polarizability. For instance we note the significant increase in conductivity upon changing from an oxygen donor (as in the platinum oxalates) to a carbon donor (as in KCP and its analogs). Second, the extent of conjugation or delocalization between atoms of the ligand remote from the donor atom must be examined more thoroughly. Third, the synthesis of materials which allow significant interchain coupling, either directly through substituents on the perimeter of the square-planar moieties, or indirectly through interaction with suitable oxidants, requires systematic investigation. A caveat should be added that ligand variations may be restricted by a possible change in the conduction mechanism, from metal-based to ligand-based.

At this point it should be pointed out that in all the theoretical treatments of conductivity and superconductivity of low dimensional metals the on-site Coulomb potential U plays an important role. High conductivity can be expected when the ratio U/t is small. It is believed that U can be reduced by surrounding the conductive metal spine by a polarizable molecular environment. This requires bulky ligands, which normally would contain a conjugated carbon substructure. With compounds containing such ligands the MM spacing can be no smaller than ≈ 3.25 Å. An important question, then, is whether significant metallic conduction can occur at such large MM spacing. Theory predicts that it can but this has yet to be confirmed by experiment. If good conductive behavior can occur with such bulky ligands it would provide the incentive for the study of a rich variety of new compounds with a large range of physical properties. These general considerations are illustrated by the recent developments in the chemistry and physics of the KCP analogues.

As outlined in some of the papers presented at this Institute there has been a great advance in the range of well characterized materials, in particular the preparation of the first anhydrous tetracyanoplatinates $\text{Rb}_2\text{Pt}(\text{CN})_4\text{PF}_6$ and $\text{Cs}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.31}$ and compounds exhibiting a much wider range of partial oxidation than seemed possible a few years ago. This very much increased range of compounds has shown the importance of:

- (i) the Pt-Pt intrachain separation on the value of the intrachain conductivity at room temperature,
- (ii) hydrogen bonding between the chains on the three dimensional ordering temperature, and
- (iii) the size of the hydrated or anhydrous cation on the intrachain Pt-Pt separation. Thus there now exists the potential for the directed synthesis of new compounds in the KCP series in which short intrachain Pt-Pt separations are combined with enhanced interchain interaction.

The anhydrous nature of some of these new compounds has removed many of the experimental difficulties associated with the study of 'hydrated' KCP. It should be stressed that what appears to be fairly small chemical changes in these series of compounds do produce very significant changes in the physical properties, and the very closely controlled chemical changes within an iso-structural series of compounds has proved particularly valuable in understanding the effects of structural changes on the electrical conductivity.

Turning to other NIOS compounds of the platinum group, work on the oxalato platinites should be aimed at the characterization of compounds with a wide range of cations, and at attempts to prepare anhydrous compounds. In the case of the partially oxidized iridium carbonyl compounds the main restriction at present is the lack of single crystals for detailed physical study. Indeed in all this area of work the growth of good quality crystals is a necessary prerequisite.

Although most of the highly conducting coordination compounds which have been thoroughly characterized are of the KCP type, several new types of highly conducting complex have been reported at this meeting. It is probable that many more such complexes can be prepared if proper combinations of the experimental parameters, described above, are selected. It is clear that a vast amount of synthetic effort is required in order to fulfill the potential of this area.

V. Nonintegral Oxidation State Complexes: Direct LL Overlap

Truly conductive NIOS systems with ligand-based transport properties have only recently been characterized. Iodine oxidation of ML complexes, where L are the highly conjugated porphyrins (P), tetrabenzporphyrin (TBP) and phthalocyanines (Pc) yields highly conductive NIOS crystals which experiment shows to have ligand-centered carriers. Preliminary studies indicate that the transport properties depend on the ligand electronic structures (MTBP vs MPc), on the intrachain separation (MTBP vs M-(octamethyl TBP)) and on the ligand size (MTBP vs MP). In addition, not only d⁸ metals, but other, including d⁰ (eg, Mg) ions give conductive systems. Finally in one case crystals with two widely different degrees of partial oxidation have been obtained, and there exists the possibilities of investigating the conductivity for a range of stoichiometries.

Comparing the results to date for the metal- and ligand-based conducting coordination compounds highlights one of the most exciting prospects provided by this field. The systematic variation of metal and ligand should permit an exploration of the nature of the dependence of crystal properties on these and other molecular features. Moreover, we might hope to find systems which span the spectrum from the extremes of metal- and ligand-dominated transport. $K_2Ni(DTO)_2$ (DTO = dithiooxalate) may be such a system.

VI. The Impact of Highly Conducting Coordination Complexes on Physics

The occurrence of materials with totally unexpected physical properties has stimulated intense studies, from which the physics society at large has profitted greatly. The impact of highly conducting coordination compounds has been felt in several areas such as one-dimensional phenomena, electron-electron coupling, pinning effects and superconductivity. Results obtained from such studies are now providing guidelines for future preparative work.

One of the greatest advances in solid state physics obtained over the last few decades is our understanding of the universal behavior of phase transitions. Critical fluctuations, i.e. precursor effects occurring close to a phase transformation, appear to be governed by only a few parameters, such as the type of interaction and the symmetry of the chemical structure. However, as the dimensionality is lowered critical fluctuations become increasingly important, and hence the extreme one-dimensional character of the conduction in these compounds has offered unusually stringent tests of the theory of critical phenomena. Also, specific to the physics of one dimensional systems is the occurrence of persistent solitary waves as opposed to ordinary harmonic wave propagation, and studies, mentioned at this Institute, are providing a opportunity to confront theory and experiment.

The coupling between electrons in condensed matter has been at issue for many years, and it is now known that the KCP type crystals exemplify a variety of cases of electron-phonon coupling in the conducting chain, and dominant Coulomb repulsion between chains. This leads to a metal-semiconductor phase transition with the appearance of an electronic charge density wave at low temperature.

Pinning effects also have recently attracted considerable theoretical attention. In one dimensional systems, pinning may arise either from disorder or from so called commensurability effects. Since compounds exhibiting both commensurate and incommensurate charge density waves in disordered materials have now been prepared, the similarity between experimental results on the two classes indicates that disorder effects dominate. Furthermore, recent studies in ordered systems show that dramatic changes occur in the electronic behavior when disorder is removed. The occurrence of $\text{Cs}[\text{Pt}(\text{CN})_4](\text{FHF})_x$, with variable x , will in the future be a key to the understanding of these effects.

One of the great challenges to the experimentalist has been the theoretical predictions that such compounds might show superconductivity at high temperatures. There are in our view two ways in which superconductivity might occur in KCP-type materials. One would be to adjust the electronic interchain coupling such that a semimetallic, rather than semiconducting phase would prevail to

temperature at which the superconductivity could occur. The other way of producing superconductivity would be to change the ligand so as to obtain an electron-exciton coupling, but this would require an increase in the intrachain Pt-Pt distance to accommodate the bulky ligands required for such exciton coupling. At present all known compounds with such large MM distance are insulators. However, experience gained from comparison of oxalato- and cyano-platinates shows that the critical distance for direct overlap metallic conduction depends upon the ligand, and therefore it cannot be ruled out that the ligands, necessary for the support of electron exciton coupling would preclude the metallic state.

VII. Conclusion

In conclusion we wish to remark on what we believe to be a major obstacle to further progress in this field. Despite the generalizations we have been able to make above, synthesis of coordination compounds with interesting collective properties remains basically a serendipitous activity. Ample expertise for preparation of new compounds exists within the chemical community, but is not being fully utilized in this field, since historically, preparative coordination chemists have concentrated their efforts on compounds of interest for their reactivity or local electronic properties, rather than on designing molecules which interact with one another in a crystal to produce novel collective states. We believe that efforts should be made to attract a wider cross-section of preparative inorganic chemists to this new science of low dimensional collective phenomena.

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