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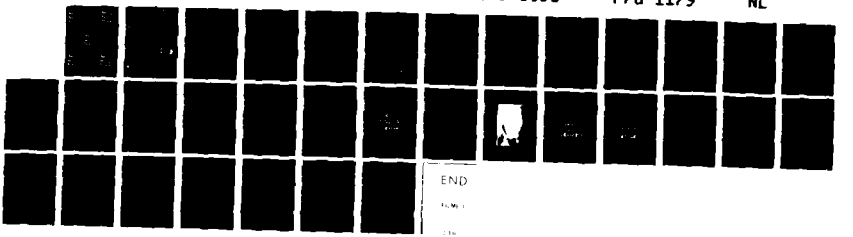

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Methods for the preparation and some of the properties of the new compounds fluoroaluminum and fluorogallium 2,3-naphthalocyanine are described. It is clear on the basis of the data gathered that these fluorides are composed of chains having metal-fluorine backbones and cofacial rings. A procedure for the preparation of iodinated species from these fluorides and some of the properties possessed by these species are described. Of particular interest are the relatively high conductivities they show when they have moderate iodine contents. It is concluded that they contain cationic chains

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Abstract

Methods for the preparation and some of the properties of the new compounds fluoroaluminum and fluorogallium 2,3-naphthalocyanine are described. It is clear on the basis of the data gathered that these fluorides are composed of chains having metal-fluorine backbones and cofacial rings. A procedure for the preparation of iodinated species from these fluorides and some of the properties possessed by these species are described. Of particular interest are the relatively high conductivities they show when they have moderate iodine contents. It is concluded that they contain cationic chains having metal-fluorine backbones and cofacial rings, triiodide and pentaiodide ions, and, possibly, uniodinated chains. Additional conclusions related to the ability of these species to conduct are discussed. Factors which in general may or do influence the conductivity of cofacial conducting polymers are also discussed.

For both theoretical and practical reasons a number of studies have been carried out on conducting polymers over the past few years. Included among the polymers studied have been a series of the cofacial, macrocyclic type (1).

The development of polymers of this type resulted from the merging of two quite different lines of investigation. One of these centered on the synthetic and structural chemistry of metal phthalocyanines and led to the discovery of $(AlPc)_2O$ (2). Later it led to the recognition of the dimeric, μ-oxo bridged nature of this compound (3).

In addition this line of investigation led to the discovery of a number of species closely related to $(AlPc)_2O$. Among these are the μ-oxo bridged oligomers AlPcOSiPcOAlPc (3), $(Me_3SiO)_2MeSiO(SiPcO)_3SiMe(OSiMe_3)_2$ (4,5), $AlPcO(SiPcO)_2AlPc$ (3), and the μ-oxo and μ-fluoro bridged polymers $(SiPcO)_n$ (6), $(GePcO)_n$ (7), $(SnPcO)_n$ (8), $(AlPcF)_n$ (9,10), and $(GaPcF)_n$ (9,10), Figs. 1 and 2.

Various studies of $(SiPcO)_n$ and its germanium and tin analogs and of $(AlPcF)_n$ and its gallium analog, including, for example, electron microscopy studies, showed that these polymers are fully crystalline, rigid-rod polymers (6,8,10,11), Fig. 3, and that their ring-ring spacings are dependent on the sizes of the atoms in their backbones (8,10). Other studies showed that the degree of polymerization of the silicon polymer can be appreciable (6).

The combinations of properties possessed by these polymers were found to be quite unusual. For example, it was found that the silicon (6), germanium (8), aluminum (10), and gallium (10) polymers are stable at high temperatures under vacuum and that the silicon polymer is inert to concentrated sulfuric acid and to hydrofluoric acid (8). The aluminum and gallium polymers (10), in contrast to the silicon (6), germanium (8), and tin

polymers (12), were found to be volatile at high temperatures, apparently because they are subject to reversible depolymerization.

The second line of investigation leading to the development of conducting cofacial polymers centered on the synthetic and physical chemistry of conducting organic species. This line of investigation revealed that $NiPcI_x$ and some other similar phthalocyanines have good conductivity when pressed into disks (13). In addition it showed that the iodinated octamethyltetrabenzporphine, $Ni(OMTBP)(I_3)_{0.36}$, contains parallel rods made of cofacially arranged rings and that it is highly conductive in the direction of its rods (14,15). Further, this line showed that $NiPc(I_3)_{0.33}$ also contains parallel rods of cofacial rings, Fig. 4, and that it too is highly conductive in the direction of its rods (16,17).

From this work it became clear that a close structural relationship exists between $NiPc(I_3)_{0.33}$ and the cofacial phthalocyanine polymers. This led to the discovery that $(SiPcO)_n$, $(GePcO)_n$, and $(SnPcO)_n$ can be oxidized with iodine and that the resulting polymers, $(SiPcOI_x)_n$, $(GePcOI_x)_n$, and $(SnPcOI_x)_n$ are good conductors (18). Soon it was reported that $(AlPcF)_n$ and $(GaPcF)_n$ can be similarly iodinated and that the polymers obtained are likewise good conductors (19).

Recently the structure of $(GaPcF)_n$ has been determined crystallographically (20), Fig. 5. As a result, both the qualitative and quantitative structural relationships for the GaPcF - $NiPc(I_3)_{0.33}$ pair are now fully known.

Other work has shown that fluorochromium phthalocyanine is a cofacial polymer too, and that iodination of it yields, not surprisingly, a conducting polymer (21). It has also been found that other oxidants can be used in place of iodine to make conducting polymers of the general type described,

e.g., bromine (18), various quinones (22), and various nitrosyls (23).

In the present work studies directed towards the synthesis and characterization of the 2,3-naphthalocyanine analogs of $(AlPcF)_n$ and $(GaPcF)_n$, i.e., $(AlNcF)_n$ and $(GaNcF)_n$, Fig. 6, and the corresponding iodinated polymers were undertaken. It was anticipated that the two iodinated polymers, if they could be made, would prove to be good conductors. (This set of uniodinated and iodinated polymers was chosen as an objective rather than one of the sets of isomeric 1,2-naphthalocyanine polymers because it was felt that the greater symmetry which these polymers would have would be generally advantageous.)

Information important to the initiation of this work was provided by three previous studies of naphthalocyanines. The earliest of these indicated that metal 2,3-naphthalocyanines could be made and that the metal-free and metal 1,2-naphthalocyanines could be isolated (24). The two later studies showed that metal-free and metal 2,3-naphthalocyanines could be isolated and yielded useful information about various members of this series including information on several aluminum and gallium species (25, 26).

Synthesis of Fluoroaluminum and Fluorogallium 2,3-Naphthalocyanine

The routes used to make fluoroaluminum and fluorogallium 2,3-naphthalocyanine were based to an important extent on procedures developed in earlier work on aluminum and gallium 2,3-naphthalocyanines (25) and phthalocyanines (10). The aluminum fluoride was made by reacting α,α,α',α'-tetrabromo-o-xylene with fumaronitrile and sodium iodide, reacting the resulting 2,3-dicyanonaphthalene with aluminum chloride, and treating the product with sulfuric acid, ammonium hydroxide, and water. Additional steps involved reacting the hydrolysis product with chlorotri-

n-hexylsilane, recrystallizing the resulting siloxide, treating the recrystallized siloxide with hydrofluoric acid, and, finally, heating the acid-treated product under vacuum. The recrystallized siloxide and the fluoride gave satisfactory elemental analyses.

The gallium fluoride was made in a generally similar way. However, tri-n-hexylsilanol was used for the preparation of the siloxide instead of the corresponding chlorosilane because use of the latter resulted in the formation of the chloride instead of the siloxide. Elemental analysis of the final product yielded satisfactory results. (The recrystallized siloxide intermediate contained some μ-oxo dimer but this did not interfere.)

Properties and Structures of Fluoroaluminum and Fluorogallium 2,3-Naphthalocyanine

The two fluorides are dark green when finely divided. They are, as expected, stable to handling and storage. They are also stable under vacuum at temperatures in excess of 500°C. However, unlike $(AlPcF)_n$ and $(GaPcF)_n$ (10), they do not sublime perceptibly at high temperatures under vacuum (this is not surprising because even iron 2,3-naphthalocyanine does not sublime readily under these conditions (27)). Both fluorides give infrared spectra of the expected kind, Fig. 7, and both give multiline X-ray powder patterns. The pattern of the aluminum fluoride has a significant line corresponding to an interplanar spacing of 3.54 Å while that of its gallium analog has a significant line corresponding to a spacing of 3.69 Å.

On the basis of the properties which these fluorides exhibit and various close relationships which they have with $(AlPcF)_n$ and $(GaPcF)_n$, it is clear that they are structural analogs of these polymers and thus are

the polymers sought as the initial objective of the work. It appears from the X-ray data that the ring-ring spacing is 3.54 Å in the aluminum polymer, and 3.69 Å in the gallium polymer. Presumably, as in the case of $(GaPcF)_n$ (20), the backbones of both $(AlNcF)_n$ and $(GaNcF)_n$ are linear, and the fluorines are situated midway between the metal atoms.

Synthesis and Nature of Iodine-Doped Fluoroaluminum and Fluorogallium 2,3-Naphthalocyanine

Fluoroaluminum and fluorogallium 2,3-naphthalocyanine doped with small to significant amounts of iodine were prepared by treating $(AlNcF)_n$ and $(GaNcF)_n$ with iodine-pentane solutions having low to substantial iodine concentrations. When the iodine concentrations were low to moderate, the iodine was taken up rapidly and quantitatively.

The iodinated products are black when they contain moderate amounts of iodine and are finely divided. They are stable to handling under ordinary conditions. Both products yield infrared spectra that show strong electronic excitation absorptions, Fig. 7, and Raman spectra that show strong lines in regions in which resonance enhanced lines for triiodide and pentaiodide ions are found (15,17,28), Fig. 8. Neither give evidence of having low molecular weights.

The currently available conductivity data for the products show that when their iodine levels are appreciable they have significant room-temperature, pressed-disk conductivities, Fig. 9. When their iodine levels are low to moderate, they have pressed-disk conductivities that are higher than those reported for their phthalocyanine analogs (29). (The conductivity observed for $(AlNcF)_n$ itself is believed to be higher than the true value. It is thought that this is due to the presence of small amounts of impurities in the $(AlNcF)_n$ used.)

On the basis of the data gathered and data available on related iodinated species (30), it is concluded that these iodinated products contain cationic chains having metal-fluorine backbones and cofacial rings, and very possibly also neutral, parent-polymer chains. The Raman data show that they contain both triiodide and pentaiodide ions. Accordingly it is apparent that these iodinated products are analogs of $(AlPcFI_x)_n$ and $(GaPcFI_x)_n$ and are the doped polymers sought.

Since the related neutral chains in $(GaPcF)_n$ are linear, the charged chains in these polymers are assumed to be linear. The charge distribution along some of them could well be nonuniform, although this is clearly open to question.

Despite the uncertainties involved, it is concluded that the charges of the chain repeat units that are charged are generally fractional. In addition it is inferred that the charges in the charged chains are associated with ligand-based orbitals and that the conductive pathways are of the ring-to-ring type.

Fluoroaluminum tetraphenylphorphine and Fluoroaluminum Octaethylporphine

As a supplement to these efforts, studies of fluoroaluminum tetraphenylporphine and fluoroaluminum octaethylporphine, a previously reported compound (31), were carried out. The tetraphenylporphine was prepared by reacting metal-free tetraphenylporphine with lithium aluminum hydride, treating the product with water, and reacting the resultant with hydrofluoric acid. Further steps involved heating the material thus obtained in a vacuum sublimator and subliming the heated product. Elemental analysis of the resulting fluoride gave values in satisfactory agreement with the theoretical values. The octaethylporphine was prepared in a similar way.

When finely divided, the tetraphenylporphine is purple while the octaethylporphine is dark red. Both fluorides are stable to handling and storage and both are relatively volatile: the tetraphenylporphine subliming at about 300 °C under vacuum and the octaethylporphine at about 270°C under vacuum. Neither, in contrast to their phthalocyanine and naphthalocyanine analogs, give powder patterns with lines that can be confidently attributed to ring-ring interplanar separations. Further, neither of them take up iodine from iodine-pentane solutions.

It thus appears that both fluorides are monomeric. This leads to the conclusion that Al(TPP)F contains square-pyramidal aluminum and, as suggested before (32), that Al(OEP)F also does, Fig. 10. Very likely the nonpolymeric nature of these fluorides is attributable to the sterically hindered nature of the ligands involved. Since these fluorides are apparently nonpolymeric and are not easily iodinated, it is concluded that it may not be easy or even possible to transform them into fluorine-bridged, cofacial conducting polymers.

Related Iodinated Cofacial Polymers

Some time ago the polymer oxogermanium hemiporphyrazine, $(GehpO)_n$, Fig. 11, was made (33). Recently the corresponding silicon polymer has been made (22). As is apparent these polymers are structural analogs of $(SiPcO)_n$ and $(GePcO)_n$. However, they differ from these polymers in that NMR data (33), X-ray data (34,35), simple Hückel considerations (36), and molecular orbital calculations (22), all suggest that the π-electrons of the ring system from which the nonbackbone portions of the polymers can formally be constructed and from which they are actually synthesized are not extensively delocalized.

Iodinated analogs of these hemiporphyrazine polymers have also been made. These analogs, in contrast to the corresponding iodinated phthalocyanine polymers, are poor conductors (22). This result is consistent with the idea that the conductivity of ring-ring conducting polymers is correlated with the amount of π-electron delocalization in the ring system from which the peripheral part of the polymers can formally be constructed (37).

Discussion

As already indicated a considerable amount of work has been done on cofacial conducting polymers apparently having fractionally oxidized repeat units and ring-ring conducting pathways. In summary, the data gathered show that in a polymer of this type a correlation exists between conductivity and level of oxidation (18,29), and suggest that in a set of such polymers correlations exist between conductivity and closeness of ring approach (18,29) and between conductivity and amount of precursor-ring π-electron delocalization (37).

As is evident, the data presented here illustrate further the correlation which exists in this type of cofacial conducting polymer between conductivity and oxidation level. They also provide additional data pointing to the existence of correlations between conductivity and ring approach and between conductivity and precursor-ring π-electron delocalization.

Whether a relationship exists between conductivity and ring size in a polymer of this type cannot be determined on the basis of the data at hand. However, it seems probable that this is the case. Similarly, whether a relationship exists between conductivity and the amount of overlap of the outer reaches of the rings also is not clear. Nevertheless, as already suggested (38), this too is likely.

On the basis of the data currently available, it seems likely that substantial electron delocalization, both along and across the chain, is necessary for high conductivity in polymers of the type under discussion. Whether the charge on the chains is associated with relatively localized or relatively delocalized orbitals is not clear.

In closing it is worth noting that these cofacial conducting polymers belong to a different class than such well-known conducting polymers as polythiazyl and doped polyacetylene (1) because the conducting pathway in the latter is along the backbone. These two classes can be distinguished by identifying the class to which the cofacial polymers belong as the conducting-ligand or conducting pendant group class, and that to which polythiazyl belongs as the conducting-backbone class.

Acknowledgment

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Figure Captions

Fig. 1. ORTEP drawing of $(Me_3SiO)_2MeSiO(SiPcO)_3SiMe(OSiMe_3)_2$ made with data gathered by Swift (5).

Fig. 2. Structure of $(SiPcO)_n$ (end groups probably OH in general).

Fig. 3. Lattice image of a $(SiPcO)_n$ crystal obtained by Linsky (11) giving evidence of the rigid-rod structure of $(SiPcO)_n$.

Fig. 4. ORTEP drawing of rod of cofacial rings in $NiPc(I_3)_{0.33}$ made with data gathered by Ibers and coworkers (17).

Fig. 5. ORTEP drawing of $(GaPcF)_n$ made with data obtained by Nohr and Wynne (20).

Fig. 6. Structure of $(AlNcF)_n$ (end group probably F in general).

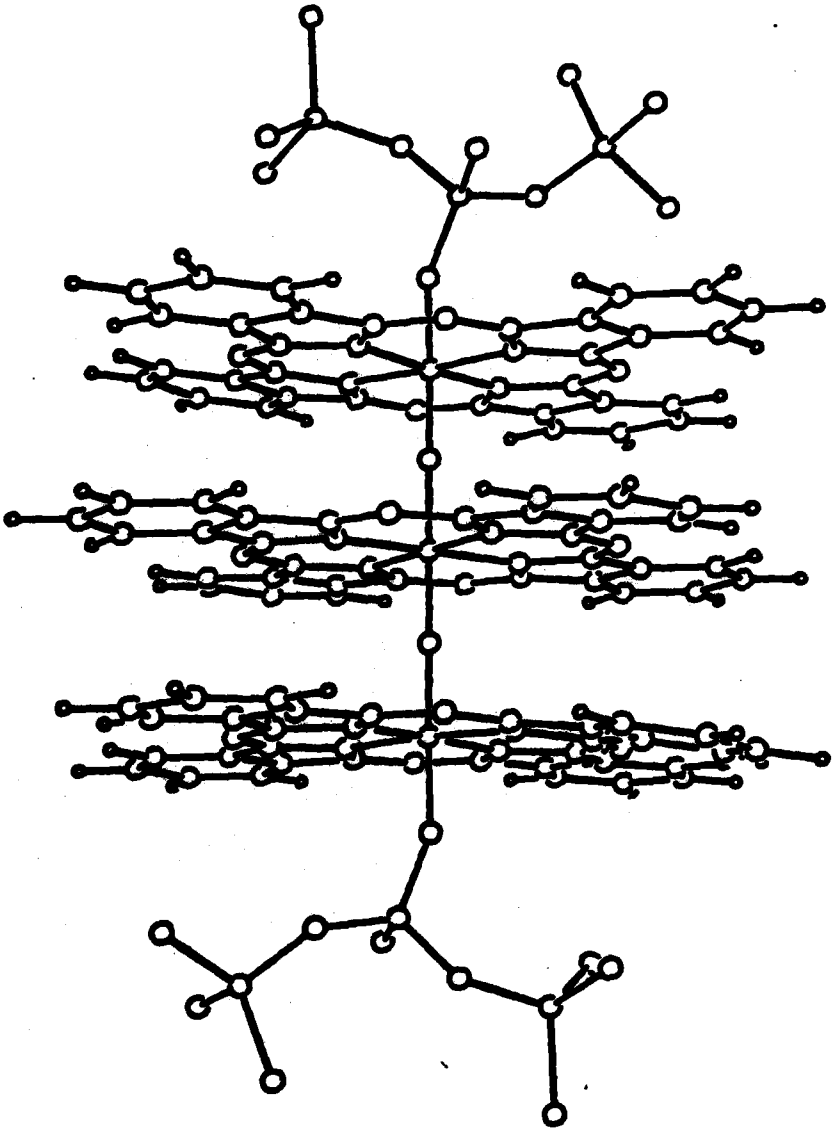
ig. 7. Infrared spectra of Nujol mulls of $(AlNcF)_n$ (top) and $(AlNcFI_{3.6})_n$ (bottom).

Fig. 8. Raman spectrum (ν_o=5145 Å) of $(GaNcFI_{1.2})_n$.

Fig. 9. Ambient-temperature, pressed-disk electrical conductivity of $(AlNcFI_x)_n$ and $(GaNcFI_x)_n$ as a function of x.

Fig. 10. Structures of Al(TPP)F and Al(OEP)F.

Fig. 11. Structure of $(GehpO)_n$ (end groups probably OH in general).



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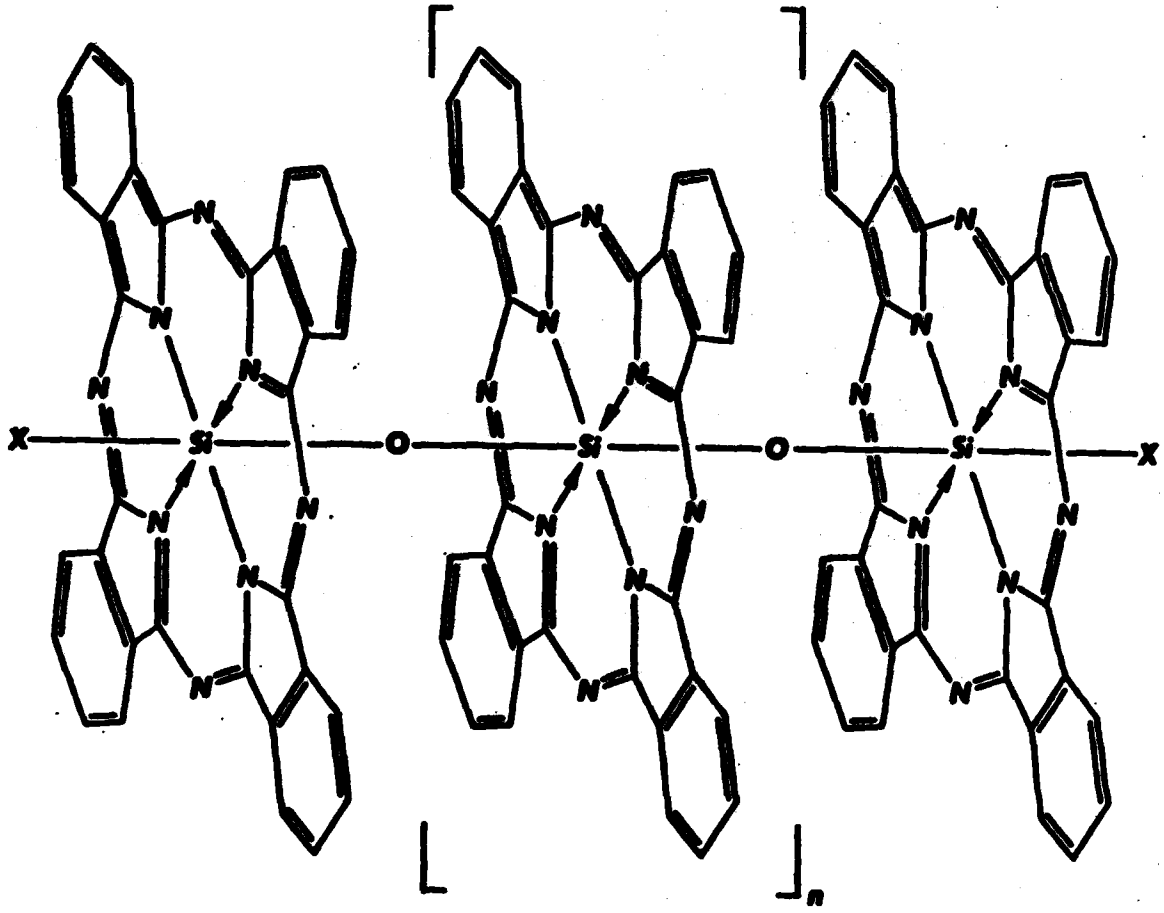
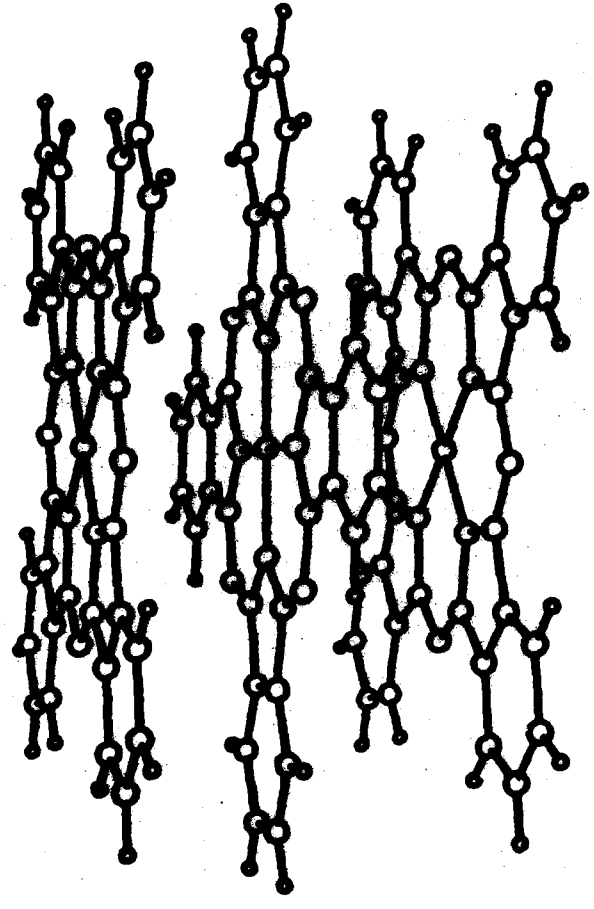


Figure 2

Figure 3



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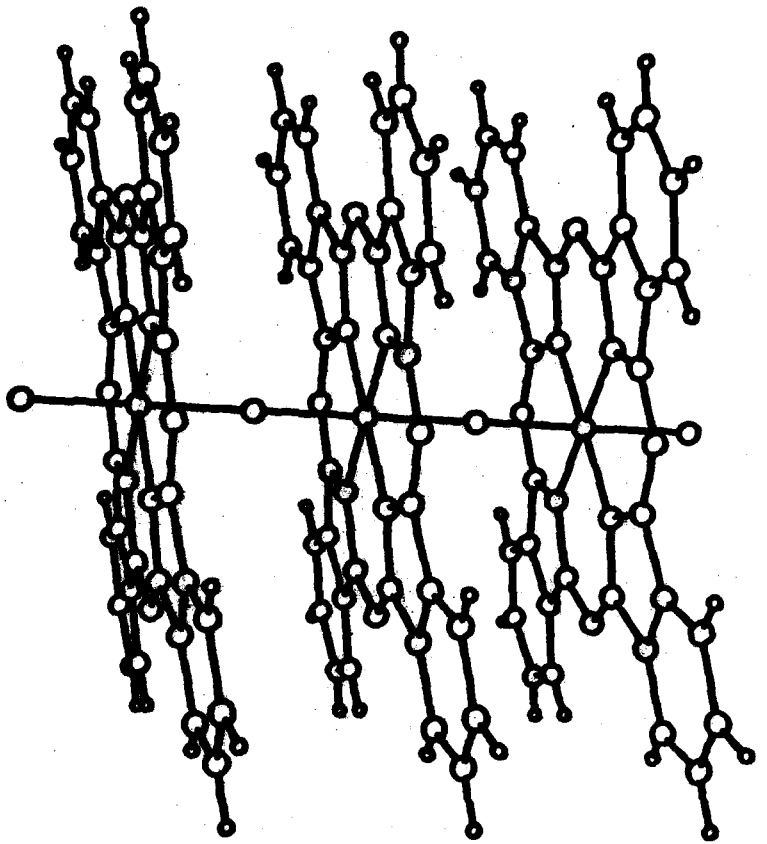

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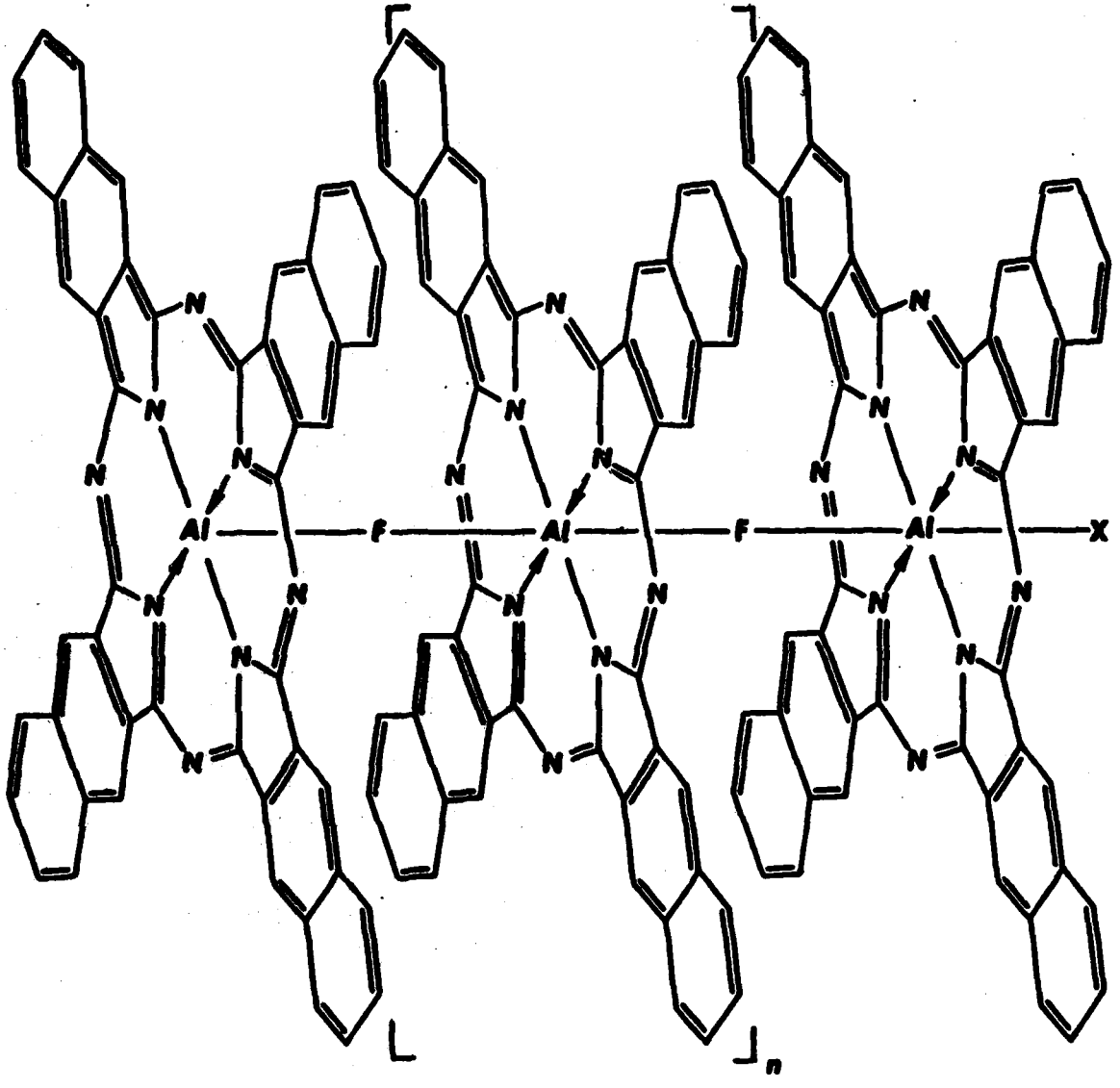

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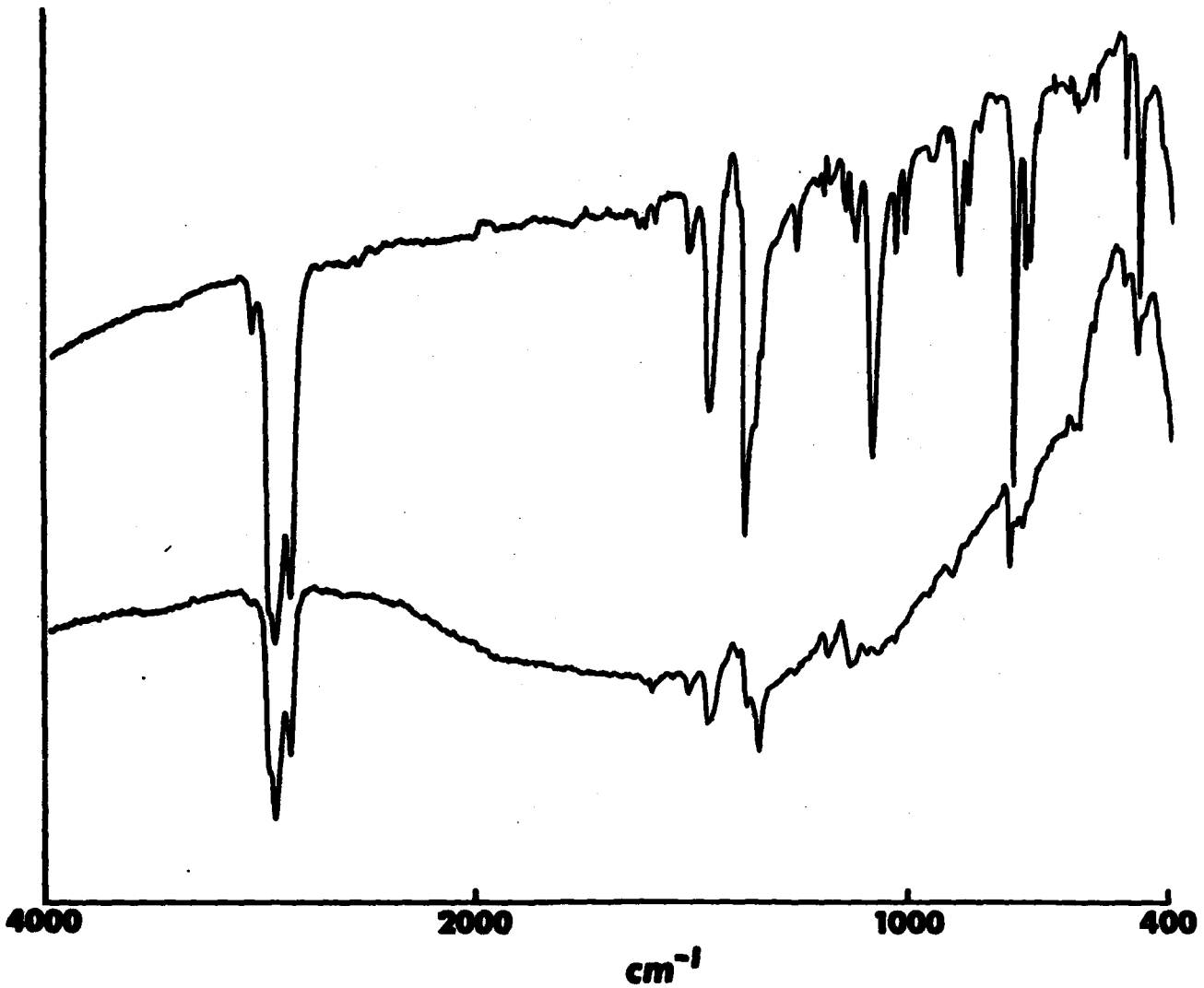

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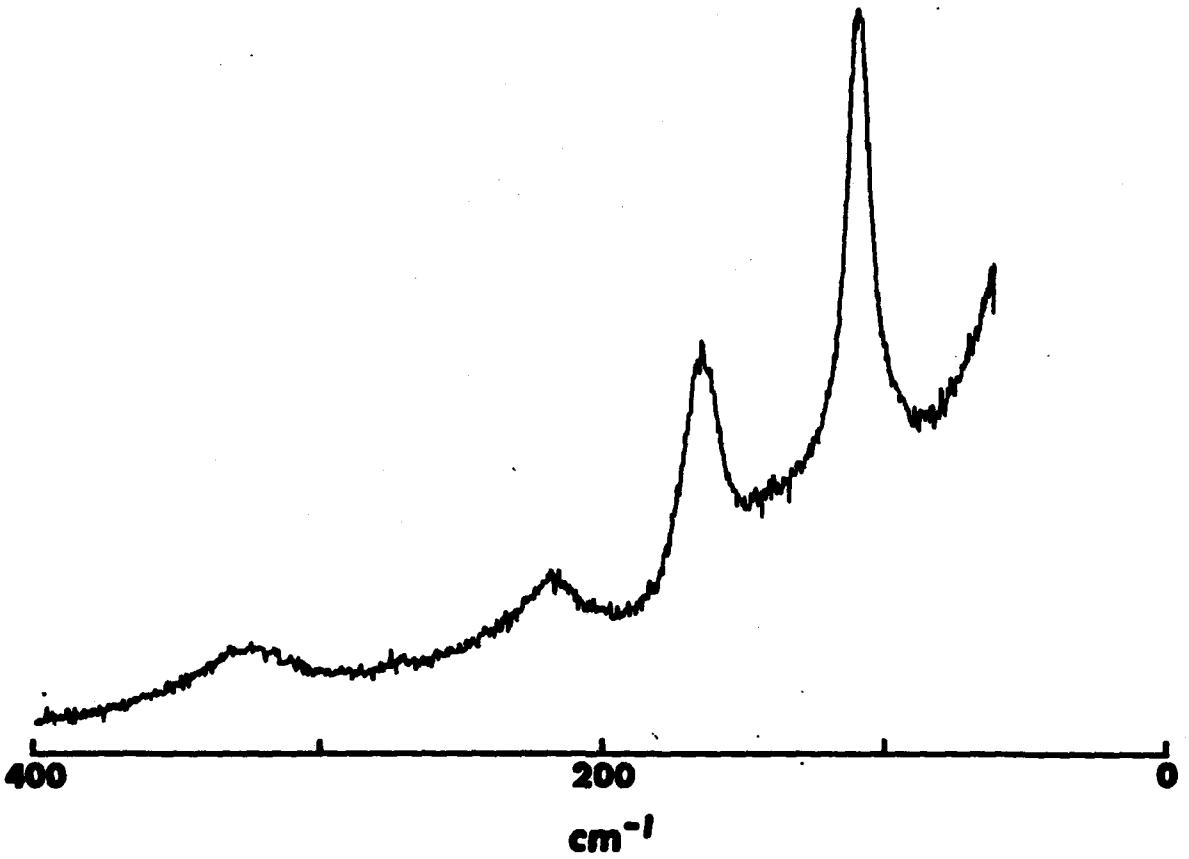

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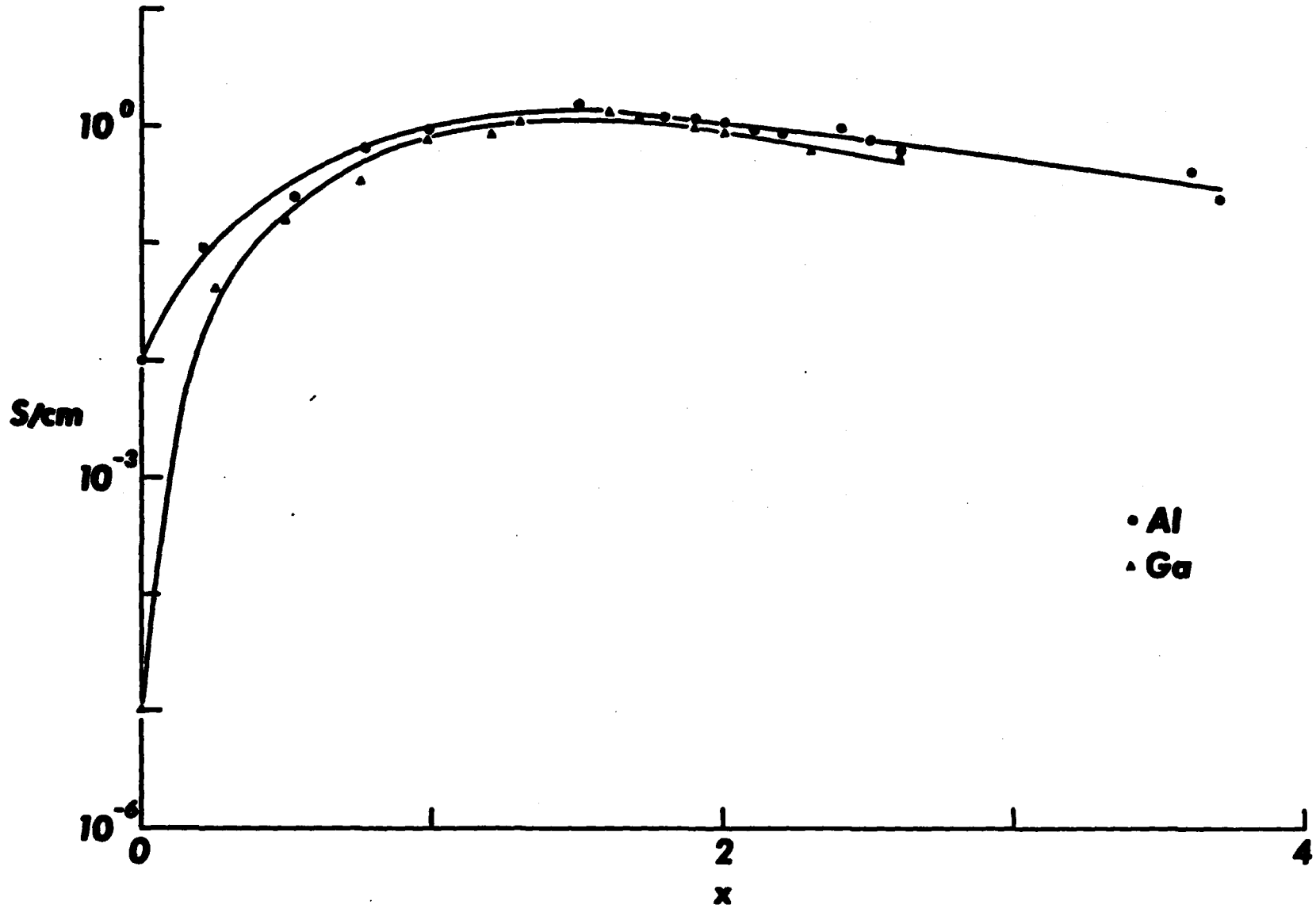
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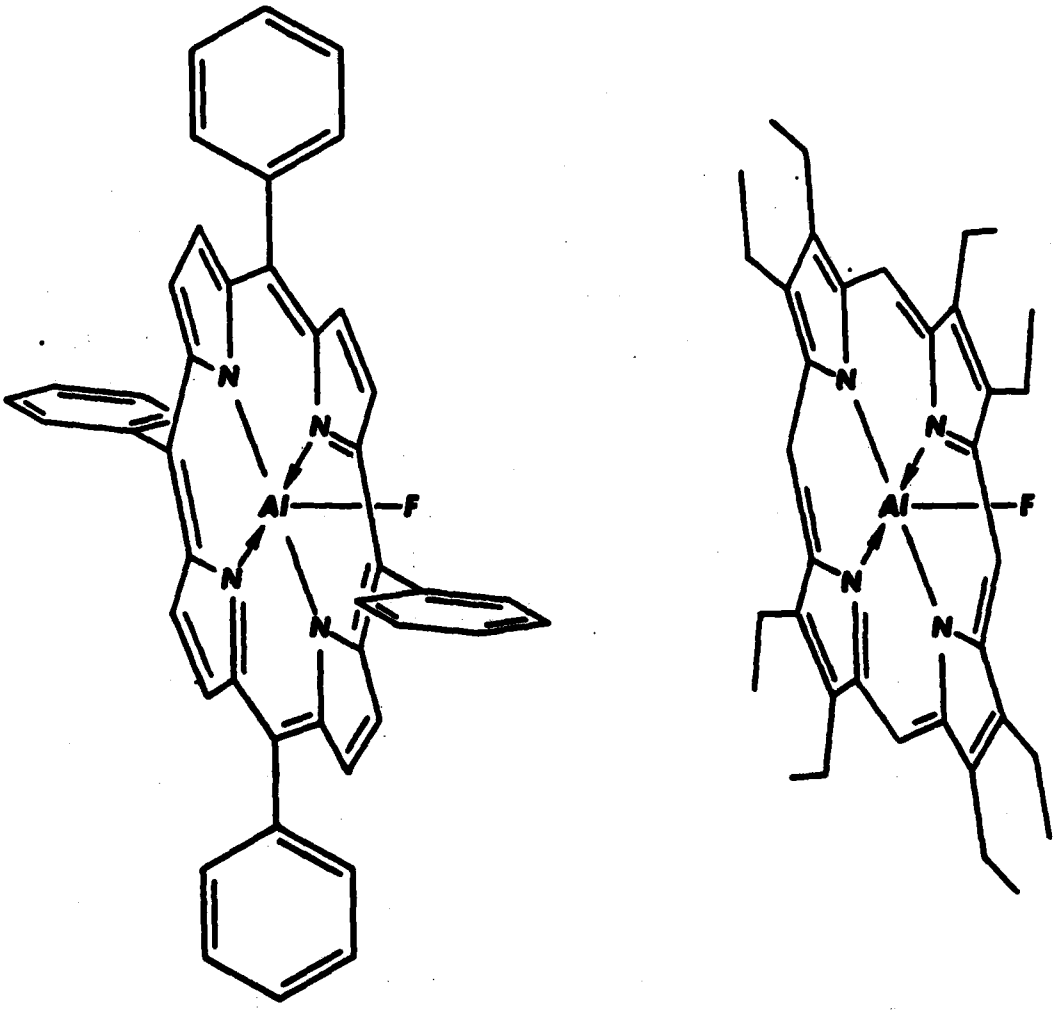

Figure 10

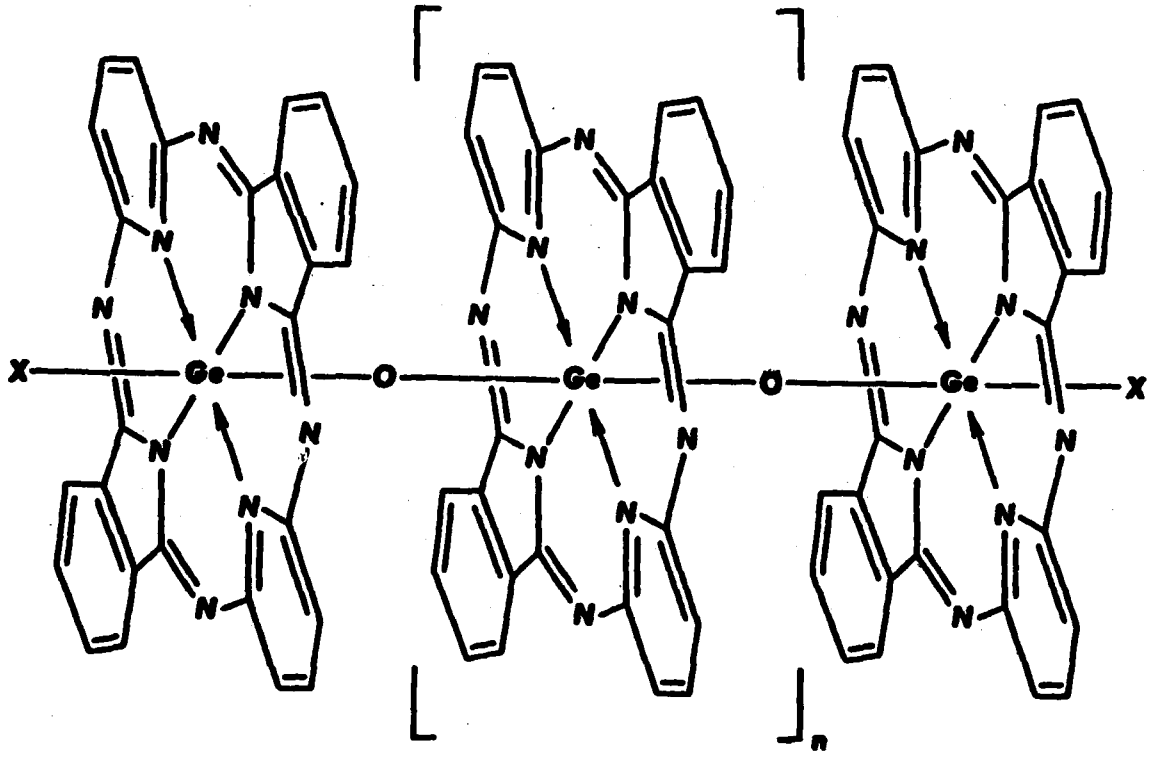

Figure 11

Question #1. Dr. Frank Ludwig, Hughes Aircraft Co.

Would you expect to get n-doping also?

Answer: Clearly this is possible and some work has been done with potassium by others. However, the resulting materials are not very stable.

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