A New Class of Charge-transfer Complexes

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Ternary charge-transfer complexes of general formula RCl–MCl_n–(aromatic compound) have been synthesized where RCl is an oxychloride such as NOCl or $POCl_3$ and MCl_n is a metal or metalloid chloride such as $SbCl_5$ or BCl_3.

The first demonstration of charge-transfer compounds was shown by the iodine–(aromatic complex) system where equilibrium constants of 1 and 6 (for concentration as mole fractions) were found for benzene and mesitylene.[1] With tetracyanoethylene as the electron acceptor equilibrium constants of 2 and 17 were obtained for benzene and mesitylene.[2]

We have prepared many charge-transfer complexes of general formula RCl–MCl_n–(aromatic compound) where RCl is either NOCl, $SOCl_2$, or $POCl_3$ and MCl_n is either BCl_3, $AlCl_3$, $GaCl_3$, $TlCl_3$, $SnCl_4$, $TiCl_4$, $ZrCl_4$, $AsCl_3$, $SbCl_3$, $SbCl_5$, or $FeCl_3$. Aromatic compounds which give these complexes include benzene, toluene, *p*-xylene, mesitylene,

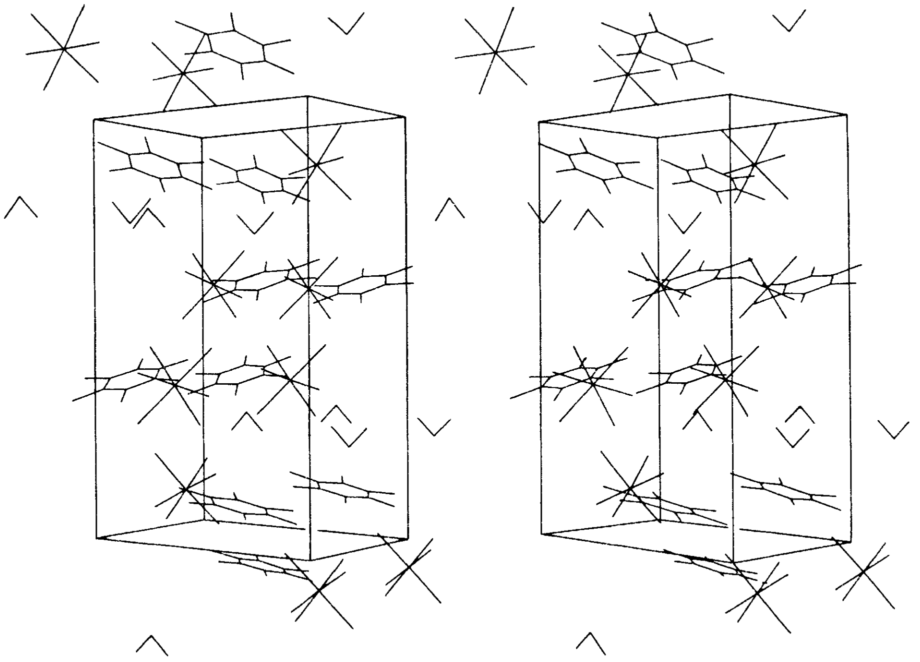

Figure 1. The unit cell of $NOSbCl_6 \cdot$ hexamethylbenzene.

hexamethylbenzene, *o*-di-iodobenzene, *p*-benzoquinone, furan, thiophene, *N,N*-dimethylaniline, naphthalene, anthracene, and polystyrene. Complex formation has been verified by u.v.–visible and i.r. spectroscopy, ^1H and ^{13}C n.m.r. spectroscopy, weight and conductivity measurements, and a crystal structure.

Both ^1H and ^{13}C n.m.r. spectra of solutions of the $NOAlCl_4$–benzene complex show rapid averaging of the signals from free and complexed benzene, even at -64 °C. Calculations based on the ^1H and ^{13}C chemical shifts as a function of the excess concentration of benzene indicate essentially complete complex formation with an equilibrium constant greater than 2 000. There is indirect evidence that stronger complexes are formed with methyl substituted benzenes than with benzene itself. Some of the $NOCl–MCl_n$ species form complexes with *p*-xylene or toluene (but not with benzene) as shown by the appearance of the colour of these complexes due to the charge-transfer absorption. An approximate order of ability to form these charge transfer complexes is $(NO)_2SnCl_6$ < $(NO)_2TiCl_6$, $(NO)_2ZrCl_6$, $NOBCl_4$, $NOAsCl_4$ < $NOAlCl_4$, $NOFeCl_4$, $NOSbCl_6$.

The proton chemical shift of hexamethylbenzene, a good electron donor, is displaced from δ 2.15 for the hydrocarbon to 2.48 ± 0.03 for complexes with $NOAlCl_4$, $(NO)_2SnCl_6$, $(NO)_2TiCl_6$, $(NO)_2ZrCl_6$, and $NOSbCl_6$. For the weaker donor, mesitylene, the change is from δ 2.23(CH_3) and 6.81(CH) to 2.58 and 7.58 for the strongly complexing $NOAlCl_4$, but only 2.47 and 7.33 for the weaker complexes with $(NO)_2SnCl_6$ and $(NO)_2TiCl_6$. It thus appears that the displacement of the chemical shift reaches a limiting value for good electron donors.

Although the equilibrium constant for charge-transfer complex formation is much greater with $NOAlCl_4$ as electron acceptor than with tetracyanoethylene there is a smaller long wavelength shift upon complex formation with $NOAlCl_4$. For benzene the shift is from 2 680 to 3 350 Å with $NOAlCl_4$ but to 3 840 Å with tetracyanoethylene.[2] Similarly for mesitylene $\lambda_{max.}$ changes from 2 820 to 3 430 Å with $NOAlCl_4$ but to 4 610 Å with tetracyanoethylene. There does not seem to be a direct relationship between the magnitude of the equilibrium constant for charge-transfer complex formation and the long wavelength shift of the absorption band. A systematic study of the chemical reactivity of these ternary charge-transfer complexes has not yet been undertaken but it was noticed that the weaker complexes were quickly decomposed to colourless products by acetone and water while some of the stronger ones were either unaffected or underwent a colour change.

Crystals of $NOSbCl_6$·hexamethylbenzene are orthorhombic in space group P_{bcm} with a = 8.2375(5), b = 19.466(2), c = 12.406(1) Å, Z = 4. 3 157 Reflections were measured with Mo-K_α monochromatized radiation, using a Picker diffractometer with profile analysis.[3] 2 382 Reflections are unique and 1 488 of these have $I_{net} \geqslant 2.5\sigma(I_{net})$. The agreement indices are R_F 0.049 (0.092, all data) and R_w 0.039 (0.039).† A view of the unit cell is shown in Figure 1. The NO moiety is disordered with the oxygen appearing at either of two positions, so it is represented in the diagram by two lines joined at an acute angle. The NO bond length is 1.43(2) Å and the nitrogen is placed nearly symmetrically at an average separation of only 2.35 Å from the six aromatic carbons. The NO bond length in this complex is much longer than that found for $NOAlCl_4$ at 0.997 Å,[4] for NO at 1.15 Å,[5] and for NOCl at 1.14 Å.[6]

The i.r. spectrum of the complex $NOSbCl_6$·hexamethylbenzene has an intense absorption band at 1 840 cm^{-1}, attributed to the N–O stretching frequency, and no other absorption at higher wavenumber until the C–H stretching frequency at 2 920 cm^{-1}. This N–O absorption is at considerably lower energy than that found for $NOSbCl_6$ at 2 189 cm^{-1}

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

and for $NOAlCl_4$ at 2242 cm^{-1}.[7] Both the *X*-ray and the i.r. results suggest considerable electron delocalization and weakening of the N–O bond.

The conductivity, between parallel plates, of a coarse, presumably single crystal, of $NOSbCl_6$·hexamethylbenzene was found to be 2.3×10^{-3} Ohm^{-1} cm^{-1} at 25 °C. In solution a single sharp proton resonance signal is observed at δ 2.41 and a signal from the carbon of the methyl groups at 16.9, but none attributed to the aromatic ring carbon atoms. An e.s.r. signal with a g value of 2.0028 was observed in the solid at 25 and −196 °C. The line width is the same at both temperatures but the intensity is much greater at low temperature with a suggestion of some hyperfine structure. These results can be interpreted in that electrical conductance in $NOSbCl_6$·hexamethylbenzene occurs *via* extensive delocalization of an aromatic π electron and an electron of the NO group in conjunction with the $SbCl_6^-$ anion but with negligible unpaired electron density at the methyl groups. The distances of 2.04 Å from the nitrogen to the centre of the aromatic ring on one side, and 3.9 Å for three of the $SbCl_6^-$ chlorines on the other side allow a possible path for current flow along the NO–aromatic–$SbCl_6$ stack.

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