ketoanilide (Cu•L) rings. However, the ternary complexes Cu•A•L are very stable. $\Delta\log[K^{Cu\cdot A}_{Cu\cdot A\cdot L} - K^{Cu}_{Cu\cdot L}]$ is positive though in Cu•β-diketone complexes Δ log K is zero. This must be because of the lone pair of electron over the anilide nitrogen, which gets delocalized over the β-ketoanilide ring. Due to increased electron density in the ring, Cu dπ orbitals do not match in energy with the β-ketoanilide pπ-orbitals in the binary Cu•L complex. In the mixed ligand complex Cu•A•L, however, mutual stabilization due to π-delocalization is more pronounced and hence there is greater stabilization. The extent of stabilization of the mixed ligand complex should depend on the π-delocalization in Cu•A. The order of π-delocalization can be expected to be Cu•dipyridyl > Cu•o-phenanthroline > Cu•2,2′-pyridyl benzimidazoline > Cu•2,2′-pyridyl imidazoline. The formation constants of the mixed ligand complexes Cu•A•L are in the same order.

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Mixed Iron and Cobalt Acetylenic Carbonyl Derivatives

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Acetylenic derivatives of mixed metal carbonyl clusters have so far received little attention [1]. Confining to the case of mixed iron and cobalt species $HFeCo_3(CO)_9(C_2Ph_2)_2$ [1], $FeCo_3(CO)_{10}C_2Ph_2^-$ and $FeCO_3(CO)_8C_2Ph_2$ [2] have been reported, but not fully characterized. We have studied the reactions of aliphatic acetylenes with iron and cobalt carbonyls by reacting in acetone the alkyne either with a preformed iron and cobalt cluster, $HFeCo_3(CO)_{12}$, or with a mixture of $Fe(CO)_5$ and $Co_2(CO)_8$. The products are substantially the same from both reactions, but they are obtained in different yields. For the alkyne being 3-hexyne the following complexes have been obtained: $Co_4(CO)_{10}C_2Et_2$, $Co_2(CO)_6C_2Et_2$, $Co_2(CO)_6EtC_2COMe$, $Co_2(CO)_6EtC_2CHOHMe$, $FeCo_2(CO)_9C_2Et_2$, $FeCo(CO)_6EtC_2CHMe$. The known cobalt derivatives have been fully characterized by m.s., i.r., ^1H and ^{13}C-n.m.r. The activation of one of the methylene groups α to the triple bond has also been observed in the products of the reaction with 4-octyne. The results of the reactions of $HFeCo_3(CO)_{12}$ with 3-hexyne in various solvents suggest that water is the source of the oxygen.

The single crystal X-ray analysis of $FeCo_2(CO)_9C_2Et_2$ shows that the complex is made of an iron and cobalt triangle with three terminal CO's bonded to each metal atom. The organic ligand is σ bonded to each cobalt atom and π coordinated to the iron one, acting as a four electron donor. The binuclear iron and cobalt derivative is obtained in low yield from the above reactions, but the yield is increased to 50% by reacting $Fe(CO)_5$ with $Co_2(CO)_6EtC_2CHOHMe$. Similarly from the reaction of iron pentacarbonyl with $Co_2(CO)_6C_2(CH_2OH)_2$, $FeCo(CO)_6CH_2OHC_2CH_2$ is obtained: in this reaction also complete dehydroxylation of the ligand occurs with transfer of the ligand from cobalt to iron to give the known $Fe_2(CO)_6CH_2C_2CH_2$ complex [3]. On this evidence and on the basis of the spectroscopic data we suggest for the $FeCo(CO)_6RC_2CHR'$ derivatives a structure in which the ligand is σ bonded to the iron atom (*via* the carbon atom previously bearing the hydroxy group) and π coordinated to the iron and cobalt atoms.

The stereochemical non rigidity of the novel complexes and of $FeCo_3(CO)_{12}^-$ will be discussed and compared with that of other iron and cobalt mixed clusters [4].

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Solute–Solvent Interaction Studies of Some Cu(II) Complexes by EPR Technique

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Even though many workers have studied solute–solvent interactions of paramagnetic complexes in solutions through the spin-Hamiltonian constants, the attempts made to find a single parameter to study the above are less. From a study on a number of Cu(II) complexes, the authors found that the amount of 4s-character present in the ground state of Cu(II) indicated the nature of the symmetry of the chromophore around Cu(II). In the present investigation six Cu(II) complexes *viz.*, (*i*) [Cu(trien)](ClO$_4$)$_2$, (*ii*) [Cu(trien)NCS]ClO$_4$, (*iii*) [Cu(trien)Br]Br, (*iv*) [Cu(trien)NCS]BPh$_4$, (*v*) [Cu(Me$_6$trien)NCS]ClO$_4$, (*vi*) [Cu(Me$_6$trien)NCS]SCN (trien = triethylenetetramine; Me$_6$trien = hexamethyltrien) in DMF (N,N'-dimethylformamide) solutions are chosen to find the validity of the above procedure. From the calculations, it is found that the ground-state of Cu(II) in the (*iv*) complex is free from 4s contribution indicating planar structure. Whereas in the case of the (*iii*) complex, the ground-state is found to possess 0.95% of 4s character indicating strong axial bond. This 4s character in other cases is found to be less than in the above complex. From these studies it is found that 1% of 4s in the ground-state has reduced isotropic contact term (K) by about 30 MHz. Using this value, the values of K in other complexes are computed and these are found to surprisingly coincide with the values obtained experimentally within 1% error.

Synthesis and Characterization of Heterometallic Clusters

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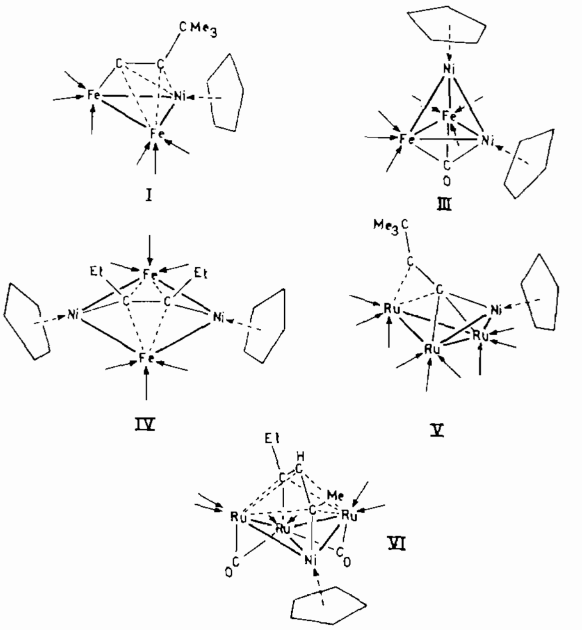
Interest towards heterometallic clusters and their reactivity is increasing [1]. Most of these species were obtained *via* redox condensation or *via* reactions of carbonylmetalates in polar solvents; some were prepared by pyrolytic reactions in apolar solvents.

We now report a synthetic method for neutral mixed clusters, based on the pyrolysis of cyclopentadienyl–nickel derivatives and of iron or ruthenium carbonyl or alkyne–carbonyl clusters, in hydrocarbon solvents. Complexes (cp)NiFe$_2$(CO)$_6$C$_2$R (R = Me [2], Bu^t [3]) (I), (cp)NiFe$_2$(CO)$_7$C·CH$_2$R (R = Me [2], Bu^t [3]) (II), (cp)$_2$Ni$_2$Fe$_2$(CO)$_7$ [4] (III), (cp)$_2$Ni$_2$Fe$_2$(CO)$_6$(C$_2$Et$_2$) [4] (IV), (cp)NiRu$_3$(CO)$_9$C·CH·Bu^t [5] (V), and two isomers (cp)NiRu$_3$(CO)$_8$(C$_6$H$_9$) [6] (VI) were characterized. The nature and yield of products is dependent from clusters stability; iron clusters are usually broken to give complexes containing two iron atoms, whereas from the ruthenium clusters mixed species, still containing three ruthenium atoms, are obtained.



The structures of the complexes (I), (III), (IV), (V) and (VI) (one isomer), determined by X-ray diffraction methods, are shown in Fig. 1.

In the above reactions, homometallic products are also obtained, as by-products; these are originated by ligand exchange (cyclopentadienyl, alkyne or carbonyl) between the two metals.

Comparable behaviour has been observed for the above compounds, in the mass spectrometer; thus comparable pyrolytic processes apparently occur in the solution and vapour phases.

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