ketoanilide (Cu•L) rings. However, the ternary complexes Cu•A•L are very stable. Δ 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.

References

1 M. V. Chidambaram and P. K. Bhattacharyia, *J. Inorg. Nucl. Chem., 32,* 3271 (1970).
2 R. Greisser and H. Sigel, *Inorg. Chem., 9,* 1238 (1970).
3 K. Gopalkrishnan and P. K. Bhattacharya, *Ind. J. Chem.,* in press.
4 Uma Doraswamy and P. K. Bhattacharya, *Ind. J. Chem., 13,* 1069 (1975).

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-$(CO)_6EtC_2CHOHMe$, $FeCo_2(CO)_9C_2Et_2$, $FeCo(CO)_6$-EtC_2CHMe. The known cobalt derivatives have been fully characterized by m.s., i.r., ^{1}H 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 $FeCo_2(CO)_9$-C_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 $Co_2(CO)_6C_2(CH_2OH)_2$, $FeCo(CO)_6CH_2OHC_2$-CH_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].

References

1 G. L. Geoffrey and W. L. Gladfelter, *Progr. Inorg. Chem.,* to be published.
2 C. G. Cooke and M. J. Mays, *J. Organometal. Chem., 74,* 49 (1974).
3 K. K. Joshi, *J. Chem. Soc.,* 594 (1966).
4 S. Aime and L. Milone, *Progr. NMR Spectroscopy, 11,* 183 (1977).

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