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Chelating Bidentate Isonitrile and Nitrile Ligands and a Few of Their Metal Complexes

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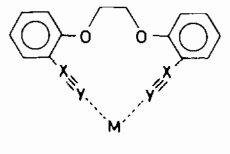
It is well-known that multidentate ligands have special properties as compared to their monodentate analogs. Yet despite considerable interest in the coordinating abilities of monodentate ligands having isonitrile ($-N{\equiv}C$), nitrile ($-C{\equiv}N$), acetylide ($-C{\equiv}C^-$), and diazonium ($-N{\equiv}N^+$) donor groups [1–4], multidentate analogs have not been explored. This is probably due to anticipated difficulties in forming a chelate ring. Molecular models indicate that a hydrocarbon chain of at least seven or eight carbons is required to link the two donor groups in such a metal chelate. However, the flexibility of such a chain might be expected to allow the formation of polymeric as well as chelated complexes. To our knowledge, the only report of a chelating ligand of this type was that used in the preparation of $Rh[CN(CH_2)_7NC]_2^+$ and $Rh[CN(CH_2)_8NC]_2^+$, where the two isonitrile donor groups are bound by a long aliphatic chain [5].

In the present communication we report the convenient synthesis of less flexible bidentate isonitrile and nitrile ligands and demonstrate by preparing several complexes of each that they readily chelate to metal ions. The ligands have the structure:



Where $-X{\equiv}Y$ is $-N{\equiv}C$, the diisonitrile ligand is abbreviated as diNC; where $-X{\equiv}Y$ is $-C{\equiv}N$, the dinitrile ligand is abbreviated as diCN. Molecular models indicate that the ligands chelate best to octahedral or square planar metal ions where the angle between the donor groups is 90°. Without considerable distortion, the ligands are not capable of tetrahedral coordination with 109° angles between the donor groups.

The dinitrile ligand (diCN) was obtained directly from the reaction of sodium *o*-cyanophenoxide with 1,2-dichloroethane in refluxing DMF (5 hr, 52% yield). It melted at 175–7 °C, and its infrared spectrum taken in CH_2Cl_2 showed a ν(CN) absorption at 2228 cm^{-1}.

The first step in the preparation of the diisonitrile ligand (diNC) involved a similar reaction (6 hr) of sodium *o*-nitrophenoxide with 1,2-dichloroethane to give the dinitro intermediate (60% yield) [6]. Reduction of the nitro groups ($Zn/CaCl_2$/78% EtOH, 90% yield) [7a], formylation of the resulting diamine (acetic formic anhydride in tetrahydrofuran, 100% yield) [7b] and dehydration of the formamide ($PPh_3/CCl_4/Et_3N$ in dichloroethane at 70 °C, 12 hr) [8] afforded the diisonitrile, diNC (m.p., 149–50 °C; IR 2126 cm^{-1} in CH_2Cl_2), which was isolated by column chromatography (silica gel/CH_2Cl_2, 70% yield).

The diisonitrile diNC ligand reacted with *cis*-$Mo(CO)_4(piperidine)_2$ [9] in acetone at room temperature (4 hr) to form pale yellow $Mo(CO)_4$(diNC) (64% yield; IR 2125 vw, 2075 w, 2010 m, 1955 s, 1945 vs cm^{-1} in hexane) [10]. The mass spectrum of $Mo(CO)_4$(diNC) exhibited a parent ion together with fragments resulting from the successive loss of four CO groups. The analogous reaction with *cis*-$W(CO)_4(piperidine)_2$ required heating (reflux, 6 hr) and gave a low yield of $W(CO)_4$(diNC) (18% yield; IR 2079 w, 2004 m, 1941 s, 1930 vs cm^{-1} in CS_2). In this case, the major product was the golden-yellow isocyanide-bridged species $[W(CO)_4(piperidine)]_2$(diNC) (78% yield; IR 2130 vw, 2104 w, 2000 s, 1935 m, sh, 1900 vs, br, 1854 m cm^{-1} in CH_2Cl_2).

The complexes, $[(C_5H_5)Fe(CO)_3]PF_6$ [11] and $[(C_5H_5)Fe(CO)_2(CS)]PF_6$ [12], reacted with diNC at room temperature (acetone solution, 5 hr) giving yellow $[(C_5H_5)Fe(diNC)(CO)]PF_6$ (86% yield; IR 2183 s, 2154 s, 2034 s cm^{-1} in CH_2Cl_2) and brown $[(C_5H_5)Fe(diNC)(CS)]PF_6$ (85% yield; IR 2173 vs, 2150 s cm^{-1} in CH_2Cl_2, 1315 vs in KBr). The molar conductance, 79.8 ohm^{-1} cm^2 mol^{-1}, of $[(C_5H_5)Fe(diNC)(CS)]PF_6$ in nitromethane is consistent with its formulation as a 1:1 electrolyte containing a chelated diNC ligand. The reaction of diNC with $Mn(CO)_5Br$ [13] in $CHCl_3$ occurred within 4 hr at room temperature to yield yellow *fac*-$Mn(CO)_3$(diNC)Br (88% yield; IR 2178 m, 2150 m, 2042 vs, 2000 s, and 1953 vs cm^{-1} in CH_2Cl_2).

The dinitrile, diCN, also forms complexes in which the ligand chelates to the metal ion. Reaction of $Mn(CO)_5Br$ with an equimolar amount of diCN in refluxing $CHCl_3$ (3 hr) gave yellow *fac*-$Mn(CO)_3$(diCN)Br (82% yield; IR 2270 w, 2226 vw, 2040 vs, 1961 s, and 1936 s cm^{-1} in CH_2Cl_2). The greenish-brown $[(C_5H_5)Fe(diCN)(CS)]PF_6$ was prepared by photolyzing (350 nm) $[(C_5H_5)Fe(CO)_2(CS)]CF_3SO_3$ and diCN in CH_3CN for 10 hr. Ion exchange in acetone on a PF_6^--containing ion exchange resin gave the product in 87% yield (IR 2270 w, 2225 vw, 1300 vs cm^{-1} in KBr). The molar conductance of this compound in nitromethane was 82.4 ohm^{-1} cm^2 mol^{-1}, which is characteristic of a 1:1 electrolyte.

Refluxing $PtCl_2(PhCN)_2$ [14] with diCN in 1,2-dichloroethane for 6 hr gave yellow $PtCl_2$(diCN) (76% yield; IR 2283 s and 2228 vw cm^{-1} KBr). That diCN displaces the monodentate PhCN ligands in this reaction illustrates the favored coordination of the chelate ligand over its monodentate analog.

These studies demonstrate that the diNC and diCN ligands readily chelate with a variety of metal ions and may be of general interest to researchers using isonitrile and nitrile ligands. We are continuing our investigations of these and other multidentate ligands containing –CN, –NC, –CC–, and $-N_2^+$ donor groups.

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