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Preliminary communication

SYNTHESES AND STRUCTURES OF NOVEL PARAMAGNETIC ORGANOMETALLIC COMPLEXES OF MANGANESE(II) AND CHROMIUM(II)

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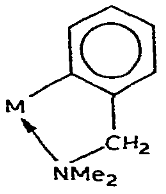
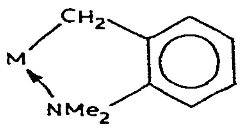
Summary

The reactions of $LiC_6H_4CH_2NMe_2$ with MnI_2 and $CrCl_2$ in tetrahydrofuran gave the air-sensitive, paramagnetic complexes $Li_2(THF)_2MX_2(C_6H_4CH_2NMe_2)_2$. The solvated lithium halide may be removed from these complexes to give $M(C_6H_4CH_2NMe_2)_2$ as paramagnetic organometallic complexes. Similarly the reactions of $LiCH_2C_6H_4NMe_2$ with $CrCl_2$ and MnI_2 gave $M(CH_2C_6H_4NMe_2)_2$ whose magnetic moments and molecular weight measurements indicate that association occurs in solution. The X-ray crystal structure of $Mn(CH_2C_6H_4NMe_2)_2$ was determined. The molecule is dimeric, containing one bridging and one terminal $CH_2C_6H_4NMe_2$ ligand per metal. The bridging ligand is bonded to both manganese atoms through a common CH_2 group. One manganese atom has a bidentate $CH_2C_6H_4NMe_2$ ligand while the other manganese atom has a monodentate *o*-dimethylaminobenzyl ligand.

Although paramagnetic organometallic compounds are relatively rare and unstable [1—3], we have found [4—8] that stabilization of these complexes can be achieved by the use of chelating organic ligands as in the generalized complexes I and II. Apart from the cyclopentadienyl derivatives few organo-



(I)



(II)

metallic complexes of chromium(II) and manganese(II) have been reported The chromium(II) complexes usually are diamagnetic, and both dimeric and monomeric compounds have been reported [9—11] Short metal—metal bond distances are observed for the dimers, and quadruple bonds are postulated to account for the diamagnetism. Beermann and Clauss in 1959 [12] reported the preparation of $MnMe_2$ and $LiMnMe_3$, which have recently been questioned by Wilkinson and coworkers [13,14] There have been only a few other reports on alkyl- and aryl-manganese(II) compounds [15,16]. We now report some unusual dimeric organometallic complexes of chromium(II) and manganese(II), which, unlike previous complexes, are paramagnetic and report also the X-ray structure of one of the manganese(II) organometallic compounds.

The slow addition of a tetrahydrofuran (THF) solution of two molar equivalents of $LiC_6H_4CH_2NMe_2$ to a suspension of one molar equivalent of $CrCl_2$ in THF at —80°C under a nitrogen atmosphere gave a dark red-purple solution. When the addition was completed, the solution was warmed gradually to room temperature, filtered, and the solvent was removed by rotary evaporation to give large, very air-sensitive, red-purple crystals which were recrystallized and analyzed* as $Li_2(THF)_2CrCl_2(C_6H_4CH_2NMe_2)_2$ (III) The magnetic moment of III determined in tetrahydrofuran, by the Evans technique [16], was 4 3 BM. Other complexes such as $Li_2(THF)_2Cr(C_4H_8)_2$ [11] and $Li_2(THF)_2$-$CrMe_4$ have stoichiometries similar to those of III except that these complexes are diamagnetic with quadruple Cr—Cr bonds postulated The large magnetic moment of III would imply the absence of any substantial multiple metal—metal bonding The thermal instability of III did not allow molecular weight measurements to be made.

The analogous manganese(III) compound, $Li_2(THF)_2MnI_2(C_6H_4CH_2$-$NMe_2)_2$ (IV), was obtained from the reaction of MnI_2 with two equivalents of LiC_6H_4-*o*-CH_2NMe_2 as a pale-yellow air-sensitive crystalline solid** The magnetic moment of IV (5.7 BM) was consistent with a six-coordinate, high-spin d^5 electronic configuration

The addition of $Li_2(THF)_2CrCl_2(C_6H_4CH_2NMe_2)_2$ to benzene caused LiCl to precipitate; the color changed to bright orange and $Cr(C_6H_4CH_2$-$NMe_2)_2$ (V) was isolated from solution in good yield as a bright orange, very air-sensitive, crystalline solid*** Unlike the similar complex bis(2-methoxyphenyl)chromium [9] which was diamagnetic, V is paramagnetic (μ_{eff}^{303} = 4.6 BM, Faraday method). In the absence of spin-orbit coupling, a magnetic moment of 4.9 BM is expected for a d^4-electronic configuration. The addition of *p*-dioxane to an ether suspension of IV rapidly precipitated LiI and $Mn(C_6H_4CH_2NMe_2)_2$ was isolated as a yellow-green, paramagnetic (μ_{eff}^{303} 5.48 BM Faraday method) crystalline solid****

The bis(benzyl-chelate) complexes, $Mn(CH_2C_6H_4NMe_2)_2$ and $Cr(CH_2C_6H_4NMe_2)_2$, were isolated from reactions of $LiCH_2C_6H_4NMe_2$

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*Anal., Found- C, 58 80, H, 7 28 Cl 13 15 N, 5 48 $Li_2Cl_2CrC_{26}H_{40}N_2O_2$ calcd - C 56 84 H, 7 34 Cl 12 91 N, 5 10%

**Anal Found- C 40 46 H, 5 45 Mn 6 38 N 3 37 $Li_2I_2MnC_{24}H_{40}N_2O_2$ calcd C 42 47: H, 5 48, Mn, 7.47, N, 3 81%

***Anal., Found: C, 67 60; H, 7 76- N, 9 21. $CrC_{18}H_{24}N_2$ calcd . C 67 47 H 7 55, N, 8 74%

****Anal . Found: C, 64 05 H, 7 78, N, 9 06 $MnC_{18}H_{24}N_2$ calcd C, 66 86 H, 7 48 N 8 67%

with MnI_2 and $CrCl_2$ as paramagnetic crystalline solids. The magnetic moment of the manganese compound was 2 6 BM.

Cryoscopic molecular weight measurements in benzene of the bis(benzyl-chelate) and bis(phenyl-chelate) complexes of both chromium and manganese indicated that some association was occurring. For example, the number average molecular weight of $Mn(CH_2C_6H_4NMe_2)_2$ (formula weight for $C_{18}H_{24}N_2Mn$ 323 3) was found to be 549 at a single concentration. This value corresponds to an equilibrium mixture containing 80% dimer and 20% monomer. Similarly, the molecular weight of V was found to be 491, corresponding to a mixture of 70% dimer and 30% monomer.

Because of the low magnetic moments and unusual molecular weights, the X-ray crystal structure of $Mn(CH_2C_6H_4NMe_2)_2$ was determined by single crystal X-ray techniques. Data were measured on an automatic diffractometer using the θ—2θ technique and Zr-filtered Mo radiation. No corrections for decomposition or absorption were deemed necessary. The structure was solved using Patterson superposition techniques. The two symmetry independent molecules were refined in separate blocks with anisotropic temperature factors for all Mn, methylene C, and N atoms and isotropic temperature factors for

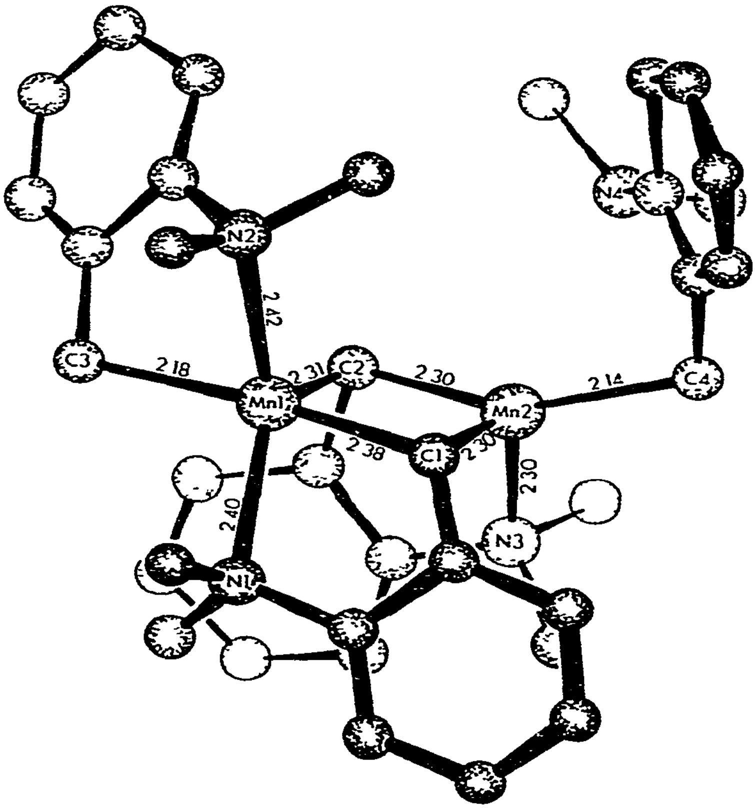
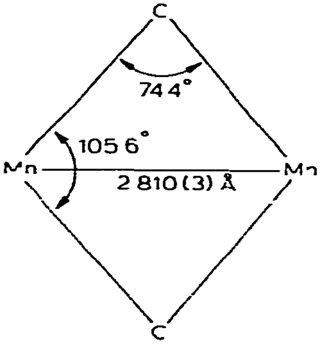


Fig.1 Molecular Structure of $Mn_2(o\text{-}CH_2C_6H_4NMe_2)_4$.

the remaining atoms. Hydrogen atoms were not included in the model at this point in the refinement The conventional *R* factor for the 2945 strongest reflections is 0.068. Crystals are monoclinic, space group *Cc*, with *a* 21 920(40), *b* 23 186(14), *c* 13.988(6) Å, and *β* 107.77(8)°. The calculated density for eight dimers per cell is 1.27 g/cm^3, we were unable to obtain an observed density

The molecular structure showing pertinent interatomic distances is shown in Fig. 1. The molecule is comprised of a dimeric unit, $Mn_2(CH_2C_6H_4NMe_2)_4$ and two symmetry-independent dimers are present. These have essentially the same structure, the main difference being that they are enantiomers The dimer is bridged by two methylene units and the NMe_2 ends of each bridging ligand are chelated to separate manganese atoms The molecule has C_2 (2) point symmetry, with the twofold axis normal to the four-membered bridging plane Mn(1) has a chelating terminal *o*-$CH_2C_6H_4NMe_2$ ligand and Mn(2) has a monodentate terminal *o*-$CH_2C_6H_4NMe$ ligand. We believe this feature may be explicable in terms of steric effects. The observed interligand methyl C···C contacts are in the 4 0—4 5 Å range; if N(4) were also bound to Mn(2), a prohibitive methyl C···C contact of less than 3 0 Å would result. Steric effects may also be at least partially responsible for differences in Mn—N and Mn—C (bridge) bond distances

We do not believe it is possible to make any definitive statement about the strength of the Mn—Mn interaction



The bridging framework is planar to 0.02 Å. Ordinarily these data would be taken to support a Mn—Mn bond [17], but the X-ray data cannot separate strong metal—metal bonding from the "bridge bonding only" case. The paramagnetism and some of the chemistry argue against a strong Mn—Mn interaction. The Mn—Mn distance here may be compared with 2.923(3) Å in $Mn_2(CO)_{10}$ [18], 2 913(6) Å in $Mn_2(CO)_8[P(C_2H_5)_3]_2$ [19], and 2 871(2) Å in $Mn_2(CO)_8(\mu\text{-}Si(C_6H_5)_2)_2$ [20].

Similar structures are probable for the aryl-chelate complexes. Further studies of the reactions and catalytic applications of these molecules are in progress.

Acknowledgments

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