Inorganica Chimica Acta, 28 (1978) L153–L154
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A Novel Mixed Ligand Complex from the Cocondensation of Cobalt Vapor with a Mixture of the Monodentate Ligand $(CH_3)_2NPF_2$ and the Bidentate Ligand $CH_3N(PF_2)_2$: The X-ray Crystal Structure of $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$

M. CHANG, M. G. NEWTON, R. B. KING and T. J. LOTZ

Department of Chemistry, University of Georgia, Athens, Georgia 30602, U.S.A.

Received March 23, 1978

We have recently [1] reported the cocondensations of iron vapor with $(CH_3)_2NPF_2$ and with $CH_3N(PF_2)_2$ to give $[(CH_3)_2NPF_2]_5Fe$ and $[CH_3N(PF_2)_2]_4Fe$, respectively. A similar cocondensation of cobalt vapor with $CH_3N(PF_2)_2$ has been found to give $[CH_3N(PF_2)_2]_5Co$ which is identical to the primary product obtained from photolysis of $Co_2(CO)_8$ with excess $CH_3N(PF_2)_2$ in diethyl ether [2] and which undergoes hydrolysis to the previously reported [3] $[(CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ upon chromatography on alumina or Florisil columns. This Communication reports the cocondensation of cobalt vapor with a mixture of the monodentate $(CH_3)_2NPF_2$ ligand and the bidentate $CH_3N(PF_2)_2$ ligand to give a novel mixed ligand complex.

Approximately 0.5 g (8.5 mg atom) of cobalt metal was evaporated over a period of 30 minutes at 0.0001 mm pressure from an alumina coated tungsten wound crucible heated electrically. The resulting vapors were cocondensed at –196 °C with an excess (~8 ml) of a 1:4 (by volume) $CH_3N(PF_2)_2/(CH_3)_2NPF_2$ mixture. Chromatography of the resulting product on Florisil using a mixture of dichloromethane and hexane gave a black band from which was isolated 0.4 g (7.5% yield) of deep violet air-stable $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, m.p. 155 °C, identified by elemental analyses (C, H, and N) and the presence of ions $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_n^+$ (n = 0, 1 and 2) in the mass spectrum. In an attempt to establish the positions of the monodentate and bidentate ligands in $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, the structure of this complex was determined by single crystal X-ray diffraction.

The complex $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$ forms tetragonal crystals: space group $P4_12_12$; $a = b = 10.578\ (3)$ Å, $c = 24.846\ (7)$ Å, Z = 8. Least squares anisotropic refinement using the 777 observed reflections ($R = 0.0471$, $R_w = 0.0482$) indicates the structure depicted in Figure 1. This structure (I: $L = L' = (CH_3)_2NPF_2$) contains a cobalt–cobalt bond bridged by the three bidentate $CH_3N(PF_2)_2$ ligands similar to the reported [3] structure of the complexes $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ (I: L = L′ = CO) and $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ (I: L = L′ = CH_3NHPF_2). The two monodentate $(CH_3)_2NPF_2$ ligands occupy the terminal L positions in this $[CH_3N(PF_2)_2]_3Co_2L_2$ system. As in the structure of $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$ a two-fold crystallographic axis passes through the NCH_3 group of one of the bridging $CH_3N(PF_2)_2$ ligands. The cobalt–cobalt bond length in $[CH_3N(PF_2)_2]_3CO_2[PF_2N(CH_3)_2]_2$ is 2.740 (3) Å as compared with 2.716 (I) Å and 2.769 (I) Å in $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ and $[CH_3N(PF_2)_2]_3Co_2(PF_2NHCH_3)_2$, respectively.

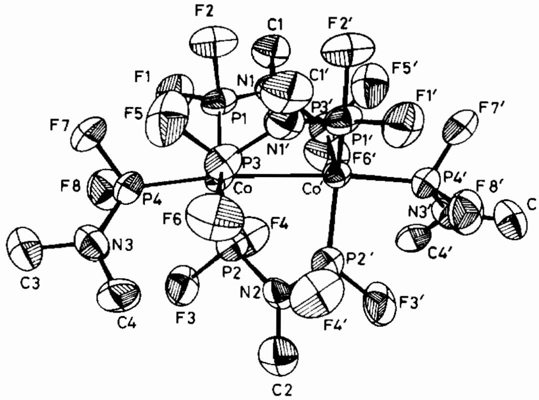
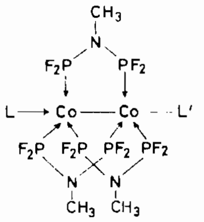


Figure 1. ORTEP drawing of the structure of $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$.



(I)

In accord with the structure I ($L = L' = (CH_3)_2NPF_2$) found for $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$, this complex was also obtained by ultraviolet irradiation of $[CH_3N(PF_2)_2]_3Co_2(CO)_2$ (I: L = L′ = CO) with $(CH_3)_2NPF_2$ in diethyl ether followed by chromatographic separation on Florisil. A by-product of this reaction is the purple unsymmetrical complex $[CH_3N(PF_2)_2]_3Co_2(CO)[PF_2N(CH_3)_2]$, m.p. 124–125 °C (I: L = CO, $L' = (CH_3)_2NPF_2$).

This work indicates that the coordinating properties of monodentate $(CH_3)_2NPF_2$ and bidentate $CH_3N(PF_2)_2$ are so different that some metal vapor reactions with mixtures of these ligands can lead to specific products rather than complex mixtures. The exclusive formation of $[CH_3N(PF_2)_2]_3Co_2[PF_2N(CH_3)_2]_2$ from reactions of cobalt vapor with the

$CH_3N(PF_2)_2/(CH_3)_2NPF_2$ mixture indicates the strong preference of bidentate $CH_3N(PF_2)_2$ for bridging metal–metal bonds and of monodentate $(CH_3)_2NPF_2$ for terminal positions.

Acknowledgment

We are indebted to the U.S. Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-75-2869. One of us (M.C.) is indebted to the University of Georgia Graduate School for a fellowship.

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