Carbon Monoxide Complexes of Macrocyclic Complexes of Cobalt(I): Synthesis and *X*-Ray Structural Characterization of Carbonyl-(6,7,13,14-tetramethyl-1,2,4,5,8,9,11,12-Octa-azacyclotetradeca-2,5,7,12,14-pentaenato)cobalt(I)

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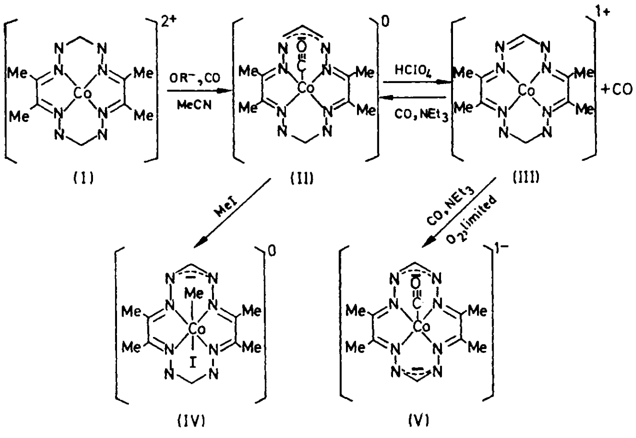
Summary A macrocyclic complex of cobalt(I) containing co-ordinated carbon monoxide has been isolated and characterized; the crystal structure reveals that the cobalt(I) is out of the plane (0·4 Å) of the macrocyclic ligand and that strong π-bonding between the cobalt(I) and the macrocyclic ligand has produced extensive delocalization in its α-di-imine chelate rings.

There is considerable interest in the co-ordination of carbon monoxide to cobalt complexes of macrocyclic ligands and other tetradentate ligands with strong planar ligand fields. Interaction of carbon monoxide with cobalt has been observed with Co^{I} in vitamin B_{12a},[1] Co^{II} with the tetraphenylporphyrin ligand,[2] and Co^{III} in dimethylglyoxime complexes[3] and other planar tetradentate ligands.[4]

We report herein the synthesis and characterization of some new Co^{II} carbon monoxide complexes, and an *X*-ray crystallographic analysis of $[Co(C_{10}H_{17}N_8)(CO)]$.

The low-spin Co^{II} compound, $[Co(C_{10}H_{20}N_8)](ClO_4)_2$ (I)[5] does not react with CO (2 atm.) at room temperature, but it does react with strong bases to produce a Co^I complex which does co-ordinate CO (Scheme). Thus, addition of Bu^tO^- (4 equiv.) or other alkoxide anions under an inert atmosphere initiates a complicated series of redox reactions in which the Co^I complex disproportionates to Co^I and Co^{III}, a process well established for other low-spin Co^{II} complexes.[6] The Co^{III} then acts as a two-electron oxidant, facilitated by deprotonation of the ligand by the alkoxide anions, introducing a double bond into one of the C–N bonds of the six-membered chelate rings. This species readily co-ordinates one molecule of CO at 1 atm. pressure to yield $[Co(C_{10}N_{17}N_8)(CO)]$, (II), δ$[(CD_3)_2SO]$: 2·12 (unresolved d, ligand Me), 4·34, (CH_2) 6·31 (N–H), and 7·93 (C–H); ν_{max} CO stretch at 1965 cm^{-1}. This diamagnetic complex undergoes typical nucleophilic reactions of Co^I and reacts with MeI to give the methyl-Co^{III} complex (IV), δ $[(CD_3)_2SO]$ 0·22 (Co–Me) and 2·30 and 2·32 (ligand Me).



SCHEME

The ability of complexes of this type to bind carbon monoxide is apparently quite sensitive to the presence of negative charge on the ligand. Protonation of the ligand, followed by the release of CO, occurs when strong mineral acids are added to (II). Addition of a base such as Et_3N under CO immediately regenerates the original Co^I–CO complex. A second double bond can be introduced into the ligand if a limited amount of molecular oxygen is present (Scheme). The Co^I–CO complex of the dianionic form of the ligand has been isolated as the triethylammonium salt, $HNEt_3[Co(C_{10}H_{14}N_8)(CO)]$, ν(C≡O) 1987 cm^{-1}.

The structure of $[Co(C_{10}H_{17}N_8)(CO)]$ was determined by *X*-ray crystallography. *Crystal data:* orthorhombic, space group *Cmca* (D_{2h}^{18}), $a = 14{\cdot}313(14)$, $b = 14{\cdot}009(9)$, and $c = 13{\cdot}720(8)$ Å; $D_m = 1{\cdot}61$, $D_c = 1{\cdot}62$ g/cm³, for $Z = 8$. A total of 2239 reflections were measured with Mo-K_α radiation to $\sin\theta/\lambda = 0{\cdot}7035$ of which 1782 independent reflections (corrected for absorption) with $F > 3\sigma$ were used in the structural refinement. Refinement of the positional and anisotropic thermal parameters for all non-hydrogen atoms by full-matrix least-squares converged to $R_1 = 5{\cdot}0$ and $R_2 = 4{\cdot}2\%$. (Hydrogen atom contributions were included in the refinement, but at fixed positions).

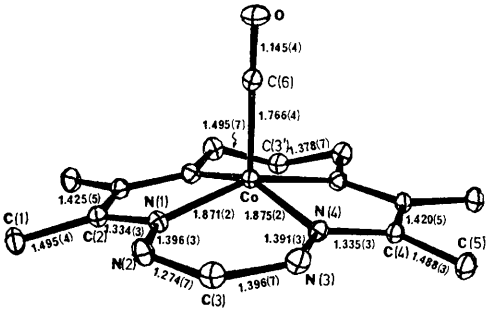


FIGURE. Structure of $[Co(C_{10}H_{17}N_8)(CO)]$, with interatomic distances in Å.

The structure is shown in the Figure.† The Co^I atom is bound to carbon monoxide and four nitrogen atoms of the monoanionic macrocyclic ligand, and is displaced 0·40 Å from the least-squares plane of the 4 donor nitrogen atoms, probably because the macrocyclic ligand core is too small to allow the Co^I to fit in the ligand plane. The Co–N bonds are very short; they are shorter than most of the metal–nitrogen distances reported for Co^{II} or Co^{III} despite the smaller radii associated with these higher oxidation states, and are indicative of the exceptionally strong π-backbonding associated with Co^I and the 'pure' α-di-imine functions of the macrocyclic ligand. The interatomic distances within the α-di-imine linkages reveal a surprising degree of delocalization, and approach the aromatic C–N distance (1·35 Å) observed in pyridine. The average 'C=N' distance, 1·333(3) Å, is significantly longer than observed in isolated co-ordinated imines (1·27 Å) or other α-di-imines (1·29 Å). The C–C distances in the five-membered rings, 1·422(5) Å, are shorter than observed in other α-di-imine structures and also approach the aromatic C–C distance (1·398 Å).

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† The molecule lies across a crystallographic mirror plane containing atoms Co, C(6), O, and which bisects the α-di-imine chelate rings. This imposed symmetry gives rise to a disordered structure in which the only slightly different halves of the molecule overlap. Thus, the accuracy of the structure, especially of those bonds involving C(3) and C(3′) is probably less than expressed by the estimated standard deviations. The figure illustrates one of the two equivalent arrangements in the lattice.

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