The Structure of a Molecular Nitrogen Compound of Cobalt and Evidence for $CoH(N_2)(PPh_3)_3$

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MOLECULAR nitrogen compounds of cobalt have recently been reported, and have been formulated both as $Co(N_2)L_3$[1,2] and as $CoH(N_2)L_3$[3] ($L = PPh_3$). We report here the first structural data on a molecular nitrogen compound of cobalt and present evidence that the compound we prepared is correctly formulated as $CoH(N_2)L_3{\cdot}Et_2O$.

The compound was prepared by the method of Yamamoto *et al.*[1] with the exception that $AlEt_3$, rather than $Al(EtO)Et_2$, was used as the reducing agent. Orange crystals were isolated from the reaction mixture at 0° in a nitrogen atmosphere. Examination of the crystals under a microscope revealed the presence of two crystal habits, one equant, the other thin prismatic. Crystals of both habits were sealed in thin-walled glass capillaries in a nitrogen atmosphere. *X*-Ray examination indicated that only crystals of equant habit were suitable for study; the thin prisms showed considerable evidence of disorder. The infrared spectrum (Nujol mull) of the mixed crystals showed two sharp peaks of very nearly equal intensity at 2085 and 2105 cm^{-1}. A single peak centred at about 2090 $cm.^{-1}$ has been assigned by previous workers to the N–N stretching mode. Only thin prisms have been made in subsequent preparations, both by the original route and by several others involving the admixture of H_2 and N_2 (in place of N_2) or of H_2 followed by N_2. In all cases the infrared spectrum (1400—2400 $cm.^{-1}$) of the product is identical quantitatively with that obtained from the original mixture of crystals. The structure of the crystals of equant habit reported here contains two molecules of diethyl ether in the unit cell. It is possible that the two modifications differ only in their ether content, and that subtle changes from our original preparative technique have prevented us from forming the ether adduct again.

The crystals of equant habit are triclinic, with cell constants $a = 12{\cdot}23$, $b = 13{\cdot}55$, $c = 15{\cdot}70$ Å $\alpha = 100{\cdot}0$, $\beta = 95{\cdot}9$, and $\gamma = 100{\cdot}3°$. The space-group was assumed to be $P\bar{1}$, and later confirmed by the successful refinement of the structure. There are two molecules of $CoH(N_2)L_3$ and two molecules of Et_2O in the cell.

Ten levels of data were recorded by precession photography ($Mo{\cdot}K_\alpha$ radiation) before the crystal decomposed. Of the 1008 non-zero intensity data estimated visually, 903 are unique. The structure was solved with difficulty by Patterson and difference Fourier techniques. Least-squares refinement of the structure was carried out with the phenyl rings treated as rigid groups. The final conventional R factor is 11·3%. The diethyl ether molecule was found in an electron density map from which the contributions of the cobalt moiety had been subtracted. The data are neither sufficiently numerous nor accurate to enable us to distinguish C from O with certainty; since the reaction was carried out in diethyl ether we consider a diethyl ether molecule of crystallization to be far more likely than a pentane molecule of crystallization. The ether molecule occupies a hole in the crystal structure; the shortest contacts are 2·7 Å to H atoms of surrounding phenyl rings.

A drawing of the co-ordination about the Co atom appears in the Figure, together with selected bond distances and angles and their estimated standard deviations. These standard deviations

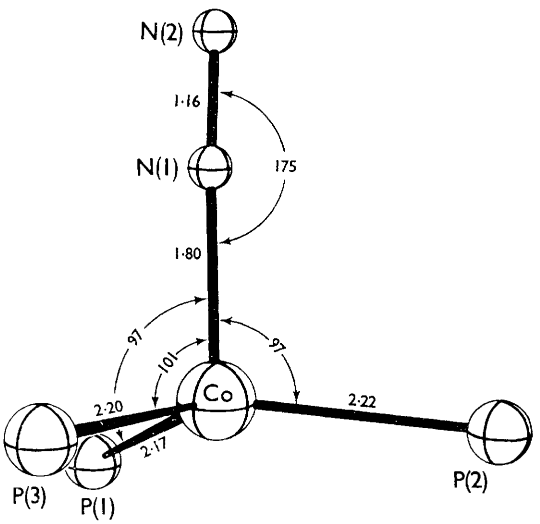

FIGURE. *Co-ordination about the* Co *atom. The* P–Co–P *angles are*: P(1)–Co–P(2) = 115·5°, P(1)–Co–P(3) = 114·6°, *and* P(2)–Co–P(3) = 123·3°, all ± 0·6°. *The standard deviations on the distances and angles in the Figure are*: Co–P, 0·02; Co–N *and* N–N, 0·04 Å; N–Co–P, 1°; *and* N–N–Co, 4°.

are large because of the limited number of intensity data. Thus a detailed discussion of the Co–N and N–N bond orders is precluded. Yet several interesting conclusions can be drawn. (i) The molecule is definitely monomeric. (ii) The Co–N–N linkage is very nearly linear, as is the Ru–N–N linkage[4] in the $Ru(N_2)(NH_3)_5^{2+}$ ion. (iii) The co-ordination about Co is best described as trigonal bipyramidal, with the Co atom 0·3 Å above the equatorial plane of the P atoms, and with one apical site apparently vacant. This configuration is identical with that found for $RhH(CO)L_3$,[5] where there was unambiguous chemical and crystallographic evidence for the presence of the H atom at the remaining apical site. Although we cannot confirm directly the presence of a Co–H bond in the present structure, we feel that indirect stereochemical evidence very strongly favours this possibility. The *ortho*-carbon atoms of the triphenylphosphine groups are far from the Co and there is no possibility of hydrogen transfer from such a carbon atom to the Co with subsequent formation of a Co–C bond. If one assumes that the H atoms are positioned normally on the C_6H_5 rings then one calculates that there are no phenyl H atoms within 3·0 Å of the Co. Consequently the apical site is not blocked by an *ortho*-hydrogen atom on a phenyl group as has been observed for $RuCl_2L_3$.[6] If an H atom is placed in the apical position 1·5 Å from the Co with an N–Co–H angle of 180°, then there are no H · · · H interactions less than 2·0 Å. Moreover, the P · · · H contacts are around 2·4 Å, to be compared with 2·5 Å in $RhH(CO)L_3$. In other words, there is room for a co-ordinated H atom. If the Co atom were only four-coordinate with tetrahedral N–Co–P angles, then the resulting P · · · P distances of 3·60 Å would in fact be longer than those of 3·56 Å which have been found[6] and so there is no steric hindrance to a tetrahedral complex. The facts that there is room for a hydrogen atom and that in its absence the complex could assume a tetrahedral configuration strongly suggest the presence of a Co–H bond and the formulation of the cobalt moiety as $CoH(N_2)L_3$.

Consequently one would expect to observe a Co–H stretching frequency, although there are examples of known hydrides that fail to exhibit a detectable metal–hydrogen stretching frequency. The only two infrared peaks observed by us between 1700 and 2200 cm.$^{-1}$ are those at 2085 and 2105 cm.$^{-1}$ noted above. It may be that these correspond to the Co–H and N–N stretching frequencies, and that previous workers failed to resolve these two peaks. Although several metal–hydrogen stretching frequencies have been observed in the 2100 cm.$^{-1}$ region, this is about 100–200 cm.$^{-1}$ higher than Co–H stretching frequencies in various carbonyl and phosphine complexes. Yet it seems possible that the Co–H stretching frequency could be higher when H is *trans* to N_2, rather than to CO.

We are continuing our attempts to prepare another crystal suitable for diffraction study. With counter data from a suitable crystal it should be possible to furnish unambiguous evidence concerning the presence of a Co–H bond.

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