Crystal and Molecular Structure of Di-iodotetrakis(phenyl isocyanide)cobalt(II). A Strictly Linear Co–I–Co Bridge

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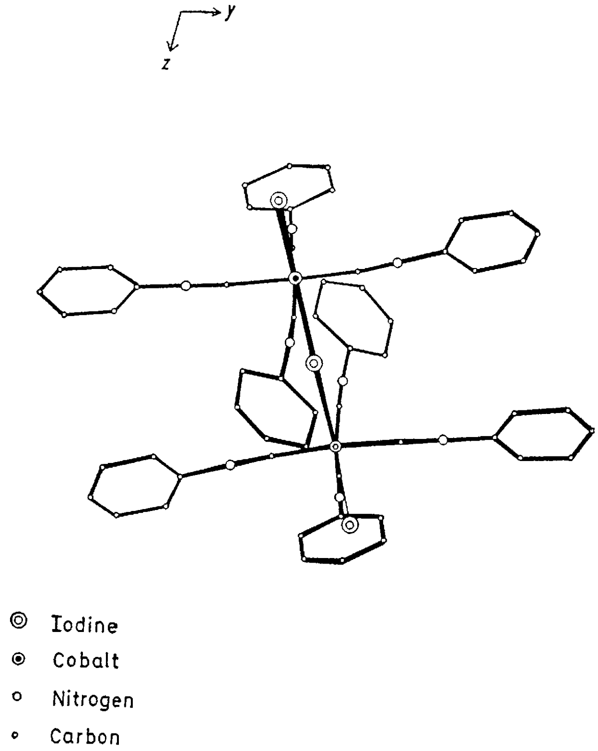
Summary The spin exchange between the cobalt(II) ions in the diamagnetic modification of $(PhNC)_4CoI_2$ is achieved through a strictly linear Co–I–Co bridge; the compound crystallizes as μ-iodo-bis[iodotetrakis(phenyl isocyanide)cobalt(II)] iodide, $[I–Co(L)_4–I–Co(L)_4–I]^+I^-$ (L = PhNC).

The surprising solid-state properties of di-iodotetrakis(aryl isocyanide)cobalt(II) complexes described first by Malatesta[1] prompted us to reinvestigate the structural features of these compounds. Whilst the structure of a *paramagnetic* complex of this type has recently been published,[2] the mechanism of spin pairing in the *diamagnetic*, deeply coloured modification of these compounds is unknown. One important question in particular is still unanswered: are there direct metal–metal bonds in the discrete dimers proposed earlier,[1] or does the spin exchange come about by way of bridging ligands and if so, what kind are they?

We prepared, therefore, diamagnetic di-iodotetrakis(phenyl isocyanide)cobalt(II) by the method described by Malatesta[1] and performed an X-ray structural analysis, which led to the ionic formula $[I\text{-}Co(L)_4\text{-}I\text{-}Co(L)_4\text{-}I]^+I^-$. The crystal data are: $[C_{56}H_{40}N_8Co_2I_3]^+I^-$; triclinic, $a = 11{\cdot}058(3)$, $b = 11{\cdot}878(3)$, $c = 12{\cdot}462(3)$ Å, $\alpha = 93{\cdot}19(2)°$, $\beta = 107{\cdot}69(2)°$, $\gamma = 104{\cdot}64(2)°$ $U = 1493$ Å^3, $Z = 1$, $D_c = 1{\cdot}621$ g/cm^3, space group $P\bar{1}$, requiring the cation to be centrosymmetric. The structure was solved by Patterson and Fourier methods. 4998 independent reflections were observed by the diffractometer method, using Mo-K_α radiation. No absorption correction was made. The structure was refined by full-matrix least-squares techniques (Co, I, anisotropic; C,N isotropic) to a conventional R value of 0·108.



Figure

The solid compound consists of discrete μ-iodo-bis[iodotetrakis(phenyl isocyanide)cobalt(II)]$^+$ cations with iodide counterions in a type of ionic lattice. The five heavy atoms in the $[\text{I–Co(CNPh)}_4\text{–I–Co(CNPh)}_4\text{I}]^+$ unit form an almost linear chain (Figure). The central iodine atom is on the symmetry centre. The angles at cobalt are 174·25(5)° but the central Co–I–Co part is strictly linear. The iodide counterion is distributed in equivalent parts over two centrosymmetrically related sites.

The iodine bridge in the cation gives rise to considerable three-centre delocalization of electrons, as indicated by the diamagnetism of the complex. The central Co–I distance in the pentanuclear heavy-atom chain is 2·890(2) Å whilst the terminal Co–I distance is 2·766(3) Å. Some literature Co–I distances are as follows. The sum of the covalent radii of Co and I is *ca.* 2·65 Å. In the tetrahedral $(p\text{-MeC}_6\text{H}_4\text{NH}_2)_2\text{CoI}_2$ the Co–I distance is 2·63 Å and in the octahedral $(p\text{-MeC}_6\text{H}_4\text{CN})_4\text{CoI}_2$ it is 2·69 Å. All Co–I distances found in the complex under discussion are surprisingly long compared to reported ones.

The structural features observed are surprising, since of the few binuclear transition-metal co-ordination compounds containing a single halogen bridge reported so far,[3,4] none has a strictly colinear metal–halogen–metal system. The comparison of this structure with other linearly binuclear transition-metal compounds containing oxygen or nitrogen bridges,[5] as discussed first by Dunitz and Orgel,[6] and with bent bridges found later by Dahl and his co-workers in the μ-iodo-bis[penta(carbonyl)chromium(0)]$^-$ anion[3] suggests that a linear Co–I–Co bridge should not occur in this binuclear co-ordination complex. In our opinion none of the proposed models[5] can really *predict* the structure and physical properties (such as magnetism) of binuclear transition-metal species, containing a single halogen bridge so a reasonable modification of the used models seems to be timely.

Another interesting point is the reported modification change to the paramagnetic form of $[\text{Co(CNPh)}_4]\text{I}_2$ which occurs even in the solid state.[1] When crystals of the α-form containing the μ-iodo-bis[iodotetrakis(phenyl isocyanide)cobalt(II)]$^+$ cations are heated to *ca.* 50 °C a slow change of colour is observed together with an increase in paramagnetic susceptibility. The isolated six-co-ordinate complex units in the lattice of the so-called β-modification[2] show that one of the ligand positions occupied by the central iodide ion is taken by the formerly 'free' iodide ion, so to speak.

$$2\,\text{Co(CNC}_6\text{H}_5)_4\text{I}_2 \rightleftharpoons [\text{I(C}_6\text{H}_5\text{NC)}_4\text{Co-I-Co(CNC}_6\text{H}_5)_4\text{I}]^+ + \text{I}^-$$

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