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The Donor Site in Indazole and other Azoles

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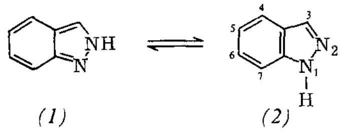
A recent paper in this journal$^{(1)}$ described the coordination chemistry of indazole ligands with respect to Ru, Rh and Ir^{III}. The structure of indazole ligands can be represented by the tautomeric equilibrium (*1*) ⇌ (*2*), and in this equilibrium, tautomer (*1*) is highly favoured over tautomer (*2*), because of the higher degree of aromaticity in (*1*).



(*1*) (*2*)

The authors of the above-mentioned paper arrive at the conclusion that the indazole ligand coordinates using N_1–H (isomer *1*). Although coordination by a – proton bearing – secondary amine nitrogen has been postulated$^{(2, 3)}$ and attacked$^{(4)}$ before, in so far such a structure has never been proven by an x-ray crystal-structure determination. Apparently, the lone pair of electrons on N_1–H is conjugated with the aromatic ring, so the lone-pair of N_2 can be active in coordination towards metal ions. In fact, all reported crystal structures of complexes containing coordinated azole ligands unequivocally demonstrate coordination of the "pyridine" nitrogen, *i.e.* the N-atom *without* a N–H group$^{(5)}$. This being the case, there is no reason to assume that indazoles would behave differently from *e.g.* pyrazoles and imidazoles. Therefore, coordination at N_2 is expected for indazoles.

Zaidi *et al.*$^{(1)}$, however, concluded that indazoles coordinate at N_1–H from the i.r. spectra in the 3000–3500 cm^{-1} region, because the N–H stretching frequency decreases. It should be realised, however, that such a decrease can have several origins, the most important undoubtedly being hydrogen bonding. This influence is most easily seen by looking at the spectral data differences on going from the solid state (strong intermolecular hydrogen bonding N–H . . . N) to a dilute solution in apolar solvents. Shifts of 200–300 cm^{-1} have been observed for several azoles$^{(6)}$.

The importance of hydrogen bonding can be nicely illustrated by examining$^{(6)}$ the i.r. spectra of $Ni(NH_3)_6X_2$ compounds, with X = Cl, Br, I, NO_3, ClO_4 or BF_4. The variation of the N–H stretching frequency in the $[Ni(NH_3)_6]^{2+}$ cation as a function of the anion, is attributed to the different hydrogen-bond acceptor properties of the anions$^{(7)}$.

Even larger anion effects have been reported for pyrazole and imidazole ligands$^{(6, 8)}$. The N–H stretching frequency for $[Ni(imidazole)_6]^{2+}$ can vary from *ca.* 3400 cm^{-1} (for the weakly hydrogen bonding perchlorate) to values as low as 2650 cm^{-1} (for strongly hydrogen bonding formate anions)$^{(8)}$. The occurrence of such hydrogen-bonding interactions has also been demonstrated by x-ray crystal-structure determinations$^{(9-11)}$.

The previous work and the i.r. spectral data of Zaidi *et. al.*$^{(1)}$ clearly indicate that indazole ligands coordinate to metal ions *via* the "pyridine" nitrogen at N_2, rather than *via* the amine nitrogen at N_1–H$^{(12)}$.

References

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