Nickel(II) Complexes of Imine Ligands derived from 7-Formylindoles

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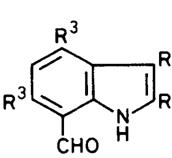
Quadridentate bis-imine nickel(II) complexes have been formed from 7-formylindoles and 1,2-diaminobenzene: an *X*-ray crystal structure determination of the chloroform solvate of the *N,N'*-bis(4,6-dimethoxyindol-7-ylidene)-1,2-diaminobenzene complex shows severe distortion from planarity and a distance of 2.96 Å between the C-2 indole atoms.

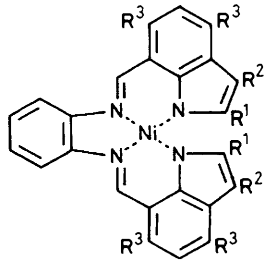
As part of our work on the incorporation of indole ring systems into new ligands for metal co-ordination, we have prepared a variety of 7-formylindoles and examined their co-ordination behaviour in some metal template reactions. 7-Formylindole (**1a**)[1] was prepared by the lithium aluminium hydride reduction of isatin-7-carboxylic acid[2] followed by dehydrogenation of the resulting 7-hydroxymethylindole with manganese dioxide. All other 7-formylindoles (**1b**—**i**) were obtained by Vilsmeier formylation[3,4] at C-7 of the related 4,6-dimethoxyindoles, which in turn were derived by means of Bischler or related syntheses.[5,6]

The 7-formylindoles can be compared with the salicylaldehydes with respect to their co-ordination chemistry and consequently the chelation of derived imines is of considerable interest. In particular, all 7-formylindoles (**1**) undergo metal template reactions with 1,2-diaminobenzene and nickel(II) acetate to yield the bright red quadridentate imine complexes (**2a**—**i**) in 40—50% yield; *e.g.* (**2b**): *m/z* 538 (100%, ^{58}Ni): ^{1}H n.m.r. δ 4.01 and 4.12, OMe; 6.12, H-5; 6.54, d, *J* 2.97 Hz, H-3; 6.81, d, *J* 2.97 Hz, H-2; 7.10 and 7.63, aryl; 8.89, imine H.

Attempts to link the two indole rings of complex (**2b**) at the C-2 positions to afford macrocyclic complexes were unsuccess-



(1)



(2)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = R^2 = H$, $R^3 = OMe$
c; $R^1 = R^2 = Ph$, $R^3 = OMe$
d; $R^1 = R^2 =$ 2-pyridyl, $R^3 = OMe$
e; $R^1 = R^2 = CO_2Me$, $R^3 = OMe$
f; $R^1 = Ph$, $R^2 = H$, $R^3 = OMe$
g; $R^1 = 4\text{-}BrC_6H_4$, $R^2 = H$, $R^3 = OMe$
h; $R^1 = H$, $R^2 = Me$, $R^3 = OMe$
i; $R^1 = H$, $R^2 = Ph$, $R^3 = OMe$

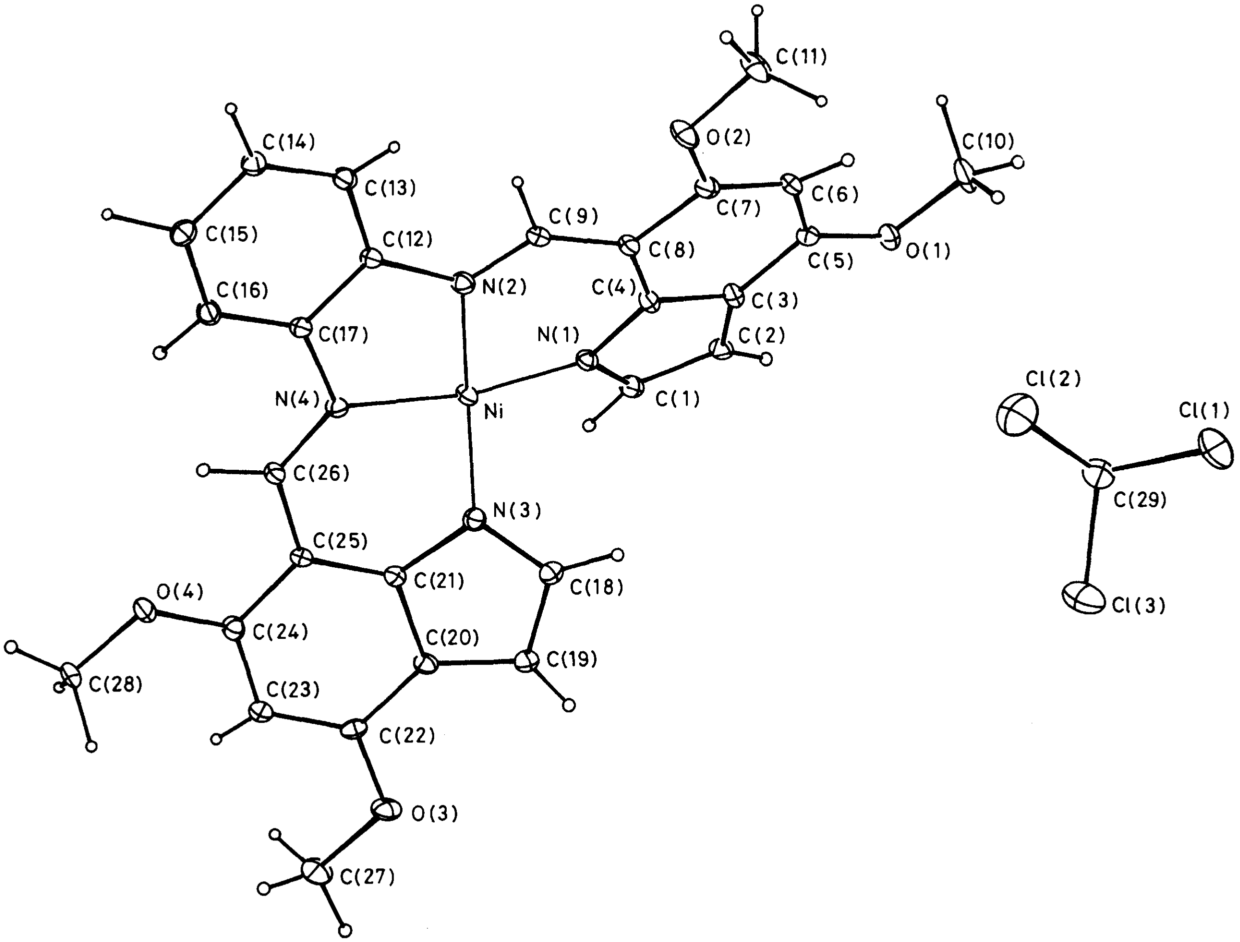


Figure 1. Molecular structure of the nickel(II) complex (**2b**). Comparison of the torsional angles (°) within the equivalent assemblages C(12)–C(17)–N(4)–C(26)–C(25)–C(21)–N(3)–C(18): −179, −178, 1, −1, and 174 respectively; and C(17)–C(12)–N(2)–C(9)–C(8)–C(4)–N(1)–C(1): −166, −171, 5, −9, and 170 respectively, indicates that the distortion of the ligand is unsymmetrical.

ful, using a variety of oxidative, reductive, thermal, and photochemical methods. In view of these results, an *X*-ray crystal structure determination of the chloroform solvate of (**2b**) was performed[†] (see Figure 1).

The most striking piece of structural information is that the distance between the two indole C-2 atoms [shown in Figure 1 as C(1) and C(18)] is 2.96 Å. It is therefore not surprising that bond formation between these two atoms has not been achieved. Indeed, the structural data show that the ligand backbone and one indole ring are relatively planar and coplanar with the nickel atom, but the second indole ring is severely twisted out of that plane. The co-ordination about the nickel is that of a distorted plane. The observed structure of (**2b**) also accounts for the fact that more hindered complexes [*e.g.* (**2c**—**g**)] could also be formed quite readily. It is noteworthy that most of the twisting from planarity is accommodated by one indole ring and not shared equally between the two. It is clear that the geometry of the quadridentate ligands is far from ideal and complex formation does not appear to be general for a wide range of metals. Complexes of cobalt(II) have been formed, but not those of zinc(II) and copper(II). Replacement of 1,2-diaminobenzene with the more flexible 1,2-diaminoethane or 1,3-diaminopropane has not so far been successful. Attempts to obtain the free imine ligand of (**2b**) have led instead to isolation of 7-(benzimidazol-2-yl)-4,6-dimethoxyindole.

A complementary approach to 2,2′-bi-indolyl ligands is reported in the following paper.[7]

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[†] *Crystal data:* $C_{28}H_{24}N_4NiO_4 \cdot CHCl_3$, triclinic, space group $P\bar{1}$ $a = 10.202(5)$, $b = 11.997(6)$, $c = 12.540(8)$ Å; $\alpha = 89.34(3)$, $\beta = 84.88(4)$, $\gamma = 66.56(5)$°; $Z = 2$, $D_c = 1.56$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 10.24$ cm^{-1}. Final R factor was 0.057 for 2407 reflections with $I/\sigma(I) \geqslant 3.0$. Intensities of 3886 data were measured in the 2θ range 3—46° for a crystal of poor quality using a Nonius CAD-4 diffractometer. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.