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# Synthesis and Structural Characterization of an Unexpected 1:1 Adduct of Nickel Diacetyl-bisbenzoylhydrazonate with *o*-Phenanthroline

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The square planar nickel(II) diacetyl-bisbenzoylhydrazonate complex, [Ni(DBH)], where $(DBH)^{=}$ is the anionic form of the $H_2DBH$ ligand, $HO(C_6H_5)C{=}N{-}N{=}C(CH_3){-}C(CH_3){=}N{-}N{=}C(C_6H_5)OH$, is capable of reacting with two molecules of unidentate bases such as pyridine, aliphatic amines, phosphines *etc.* to form hexa-coordinated adducts of the type $[Ni(DBH){\cdot}L_2]$. The thermodynamics of formation of many such adducts was thoroughly studied and a large knowledge of the basic strength of several series of amines as well as of the binding capability of phosphines as compared with that of amines was obtained [1].

Now we have found that the [Ni(DBH)] complex reacts with *o*-phenanthroline in ethanol solution to give an 1:1 adduct. Owing to the geometry of the *o*-phenanthroline molecule (having the two nitrogen atoms in a chelating position) neither a polymeric compound formed by an *o*-phenanthroline bridging two [Ni(DBH)] molecules, nor a monomeric hexacoordinated [Ni(DBH)·*o*-phenanthroline] adduct with an *o*-phenanthroline in a *cis* position can be conceived.

In order to obtain decisive information about the stereochemistry of the adduct a complete X-ray analysis was carried out.

## Experimental

The adduct was prepared by reacting an ethanolic solution of [Ni(DBH)] complex (1 mmol in 20 ml ethanol) with an ethanolic solution of *o*-phenanthroline (1.2 mmol in 5 ml ethanol). The brown crystals of the compound, which are obtained at room-temperature, were washed with ethanol and dried under vacuum. *Anal.* Calcd. for $C_{34}H_{36}NiN_6O_4$: C, 62.69; H, 5.57; N, 12.90; Ni, 9.01. Found: C, 61.34; H, 5.62; N, 12.56; Ni, 9.25.

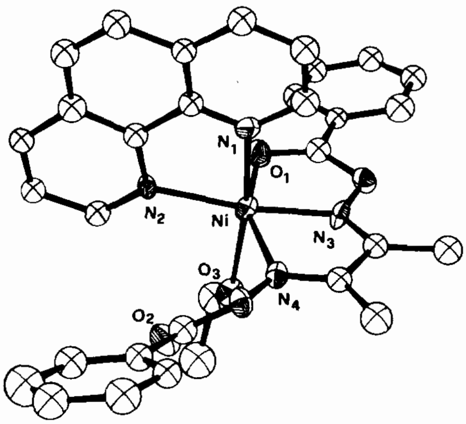

Figure 1. Perspective view of the [Ni(HDBH)(*o*-phenanthroline)(ethoxy)] complex molecule (ORTEP diagram showing 30% probability ellipsoids).

TABLE. Bond Lengths (Å) and Angles (deg) in the Coordination Polyhedra.

| | I Molecule | II Molecule |
|---|---|---|
| Ni–N1 | 2.070(25) | 2.113(29) |
| Ni–N2 | 2.086(12) | 2.108(12) |
| Ni–N3 | 1.989(12) | 1.973(12) |
| Ni–N4 | 2.121(11) | 2.119(10) |
| Ni–O1 | 2.121(10) | 2.103(9) |
| Ni–O3 | 2.076(21) | 2.095(22) |
| N1–Ni–N2 | 80.2(7) | 76.8(7) |
| N1–Ni–N3 | 92.4(7) | 97.1(7) |
| N1–Ni–N4 | 88.5(7) | 91.6(8) |
| N1–Ni–O1 | 97.4(6) | 95.8(7) |
| N1–Ni–O3 | 166.4(6) | 167.4(8) |
| N2–Ni–N3 | 170.1(5) | 172.1(5) |
| N2–Ni–N4 | 108.0(4) | 107.6(4) |
| N2–Ni–O1 | 97.7(4) | 98.2(4) |
| N2–Ni–O3 | 92.1(7) | 95.2(6) |
| N3–Ni–N4 | 78.1(4) | 77.3(4) |
| N3–Ni–O1 | 76.6(4) | 77.3(4) |
| N3–Ni–O3 | 96.4(7) | 91.6(7) |
| N4–Ni–O1 | 154.2(4) | 154.2(4) |
| N4–Ni–O3 | 83.2(7) | 81.4(7) |
| O1–Ni–O3 | 94.7(6) | 95.0(6) |

## Crystal Data

The crystals are monoclinic, space group *C*2/*c*, $a = 32.82(2)$, $b = 16.18(1)$, $c = 24.58(1)$ Å, $\beta = 103.0(1)°$, $D_c = 1.36$ gcm$^{-3}$ for $Z = 16$, $\lambda$(Mo-K$\alpha$) = 0.7107 Å, $\mu$(Mo-K$\alpha$) = 6.568 cm$^{-1}$.

Intensity data of 2982 observed, symmetry independent reflections in the range $6° \leqslant 2\theta \leqslant 40°$ were collected on a Philips PW 1100 automatic computer-controlled diffractometer. The $\omega{-}2\theta$ scan technique was used with a scan speed of 0.08°/s in a range of 0.8° across the peak. Background counts were collected at the extremes of the scan for 0.5 times the time used for the scan itself. The structure analysis which required the determination of the parameters for two independent unit-formulae of the adduct was solved by three-dimensional Patterson–Fourier methods. A difference Fourier map calculated at $R$ value 0.12, clearly showed the presence of some molecules of ethanol in the cell. Since two of these ethanol molecules are astride symmetry elements, their multiplicity is 0.5. Hydrogen atoms were introduced in their geometrical calculated positions (C–H = 0.95 Å) and not refined. The structure was refined by block-diagonal least-squares to $R$ and $R_w$ values of 0.066 and 0.077 respectively. Anisotropic thermal vibrations were assumed for nickel, oxygen and nitrogen atoms.

In Figure 1 a perspective view of one of the two independent molecules is shown. The Table reports bond lengths and angles in the coordination polyhedra.

The crystal and molecular structure consists of [Ni(HDBH)(*o*-phenanthroline)(ethoxy)] complex molecules, two molecules of ethanol as solvent also being present in the asymmetric unit. The geometry of coordination about the nickel atom is a distorted octahedron with very little difference in the two complex molecules. The $(HDBH)^-$ ligand acts as a tridentate ligand being coordinated to the central nickel by two nitrogen atoms and by the oxygen atom of one benzoyl group. These three donor atoms occupy three corners of the octahedron in a *meridional* configuration. The other benzoyl group in enolic form is a non-coordinating free arm (Ni···O2 = 3.284(9) and 3.317(9) Å respectively in the two complex molecules). Two other *cis* positions in the coordination polyhedron are occupied by the two nitrogen atoms of the *o*-phenanthroline molecule, while the sixth vertex of the octahedron is occupied by the oxygen atom of one ethoxy group. The free benzoyl group of the $(HDBH)^-$ ligand is involved in a hydrogen bond system with an ethanol molecule, as appears from the short contact distances $O2\cdots O_{solv}$ = 2.83(1) and 2.64(1) Å respectively in the two complex molecules [3, 4]. The loss of the crystallographic equivalence between the two independent molecules appears due to the different orientation of the ethanol molecules which are hydrogen bonded to the free benzoyl groups. There are no anomalous bond angles or distances in either of the independent molecules.

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