Inorganica Chimica Acta, 25 (1977) L51–L52

Bis(difluoroborondimethylglyoximato)nickel(II) and Its 1:1 Aniline Adduct

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Received September 13, 1977

Several recent studies on the chemistry of metal complexes of *vic*-dioximes have centered on their application to areas such as structure [1], biochemical models [2, 3] and semiconducting properties [4, 5]. The structures of the nickel(II) complexes of substituted glyoximes often involve Ni–Ni one-dimensional chains [6] that are said to give rise to the high stability and semiconducting nature of these compounds [4]. In the case of the dimethyl-substituted complex, $Ni(dmgH)_2$, reaction with BF_3 leads to substitution of the O···O bridging protons by BF_2 groups that allows the macrocyclic square-planar product to accommodate additional ligands in one or both axial positions [7]. The resulting complexes however retain the diamagnetic character of the parent.

Graddon and Siddiqi [8] have studied the interaction in solution of several monodentate bases with BF_2-substituted complexes of this form, noting that there is evidence only for the formation of five-coordinate 1:1 adducts under these conditions. We have isolated a series of such complexes with several glyoxime substituents and various nitrogenous monodentate and bidentate bases [9]; diamagnetic 2:1 adducts are readily isolated with the monodentate bases chosen. An exception is the group of 1:1 complexes formed with aniline and substituted anilines.

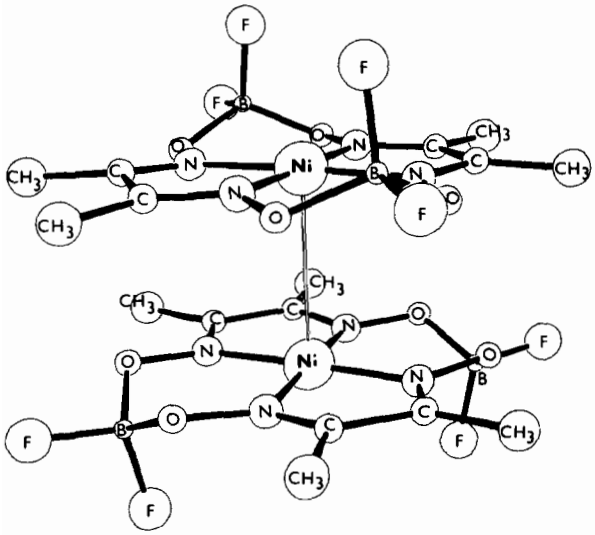

Fig. 1. Molecular structure of $[Ni(dmgBF_2)_2]$.

The crystal structure of $[Ni(dmgBF_2)_2]$ [10] shows the planar complex to be dimeric in the solid state with a Ni–Ni interaction of 3.21 Å, some 0.04 Å shorter than the corresponding distance in the chain structure of the parent [11], and with the two BF_2 groups of each unit adopting a *cis* configuration to the molecular plane (Fig. 1). This dimeric nature is retained in nitrobenzene solution, where the M.W. was found to be 686 (calc. 769 for dimer) by freezing-point depression measurements. No mass-spectral evidence could be obtained for species in the gas phase of mass greater than the monomer.

Preliminary results on the crystal structure of the 1:1 aniline adduct, $[Ni(dmgBF_2)_2(an)]$, show that this dimeric character is retained upon coordination of the base (Fig. 2), which may be true also for the species observed by Graddon and Siddiqi [8].

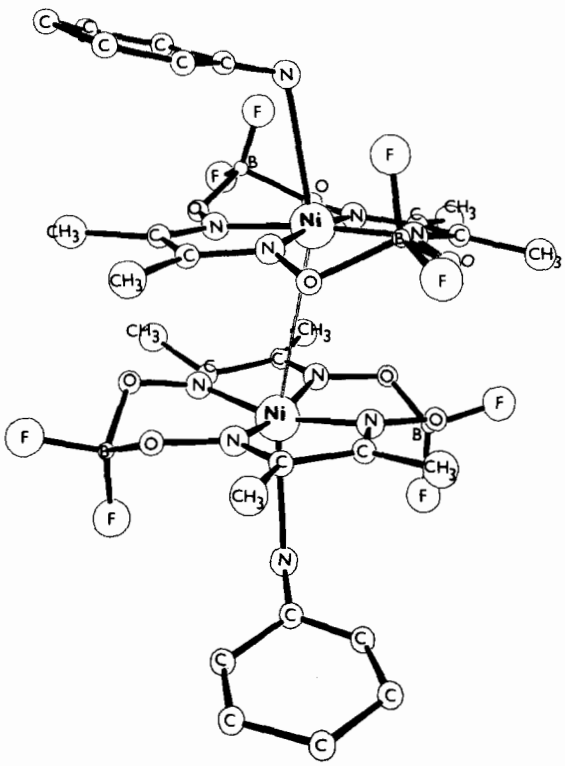

Fig. 2. Molecular structure of $[Ni(dmgBF_2)_2(an)]$.

As in the parent structure (Fig. 1) the two macrocyclic glyoxime residues are rotated approximately at right angles around the Ni–Ni direction. However there is a 0.47 Å increase in the Ni–Ni length to 3.68 Å together with a small translation of the two

macrocyclic rings relative to each other. Small deviations in the latter from the planarity found in the parent structure are evident also. The in-plane Ni–N bond lengths (av. 1.87 Å) are the same as in [Ni(dmgBF$_2$)$_2$] [10] and contrast with the axial Ni–N$_{aniline}$ average distance of 2.71 Å. This long Ni–N distance, together with the compound's diamagnetic character and the observation [8] that only 1:1 adducts of relatively low thermodynamic stability were apparent in solution, suggests that any interaction between the base and the metal atom is weak. The molecular structure of the adduct resembles in many ways that reported by Caulton and Cotton [12] for the compound [Rh(dmgH)$_2$(PPh$_3$)]$_2$.

With the bidentate bases 1,10-phenanthroline, 2,2′-bipyridyl and 1,2-diaminoethane paramagnetic 1:1 adducts usually result [9]. The crystal structure of [Ni(dpgBF$_2$)$_2$)(*o*-phen)](acetone)$_2$ (dpg is the diphenylglyoxime residue) shows the macrocyclic ligand to be severely distorted from planarity, resulting in an irregular octahedral coordination to the metal atom [13]. The dark-red complex formed with [Ni(dmgBF$_2$)$_2$] and the potentially bidentate ligand *o*-phenylenediamine however is diamagnetic. A preliminary crystallographic study suggests that in this compound the base may be functioning as a monodentate in a fashion similar to the aniline compound described above.

A further interest in complexes of this form arises from the antitumour activity exhibited for Cu(II) and Pd(II) chelates of mono- and dimethylglyoximes [14–16]. Because of its solubility in organic solvents [Ni(dmgBF$_2$)$_2$] has been tested as a potential antitumour substance. However, similar to the unsubstituted Ni(dmgH)$_2$, the compound proved to be inactive in both the leukaemia L1210 and KB cell-culture test-systems.

Experimental

The deep-scarlet crystalline complex [Ni(dmgBF$_2$)$_2$(an)] forms readily from the reaction of aniline with [Ni(dmgBF$_2$)$_2$] in warm dichloromethane. *Anal.* Found, C 35,3; H 4.1; N 14.5%. Calc. for C$_{14}$H$_{19}$B$_2$F$_4$N$_5$NiO$_4$: C 35.2; H 4.0; N 14.7%. The adduct reverts to the yellow parent with loss of base when heated to 115 °C (Wt. Loss: Found, 19.4%. Calc., 19.5%).

Crystal Data

[Ni(dmgBF$_2$)$_2$(an)]: C$_{14}$H$_{19}$B$_2$F$_4$N$_5$NiO$_4$, monoclinic, a = 20.21(4), b = 9.94(2), c = 19.41(4) Å, β = 95.9(2)°, Z = 8, space group $P2_1/c$.

At present the structure has been refined isotropically to R = 0.10 for 1470 visually estimated non-zero reflexions (35% of data collected). Details of the full structure analysis, when completed, will be reported in a future article.

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