# The role of transition metal ions in hydrogen bonded networks: a density functional molecular orbital theory study

**John E. McGrady and D. Michael P. Mingos** *

*Department of Chemistry, Imperial College of Science, Technology and Medicine,*
*South Kensington, London, UK SW7 2AY*

**The capacity of biureto- ($C_2N_3O_2H_3^{2-}$) and dithiobiureto- ($C_2N_3S_2H_4^{1-}$) complexes of nickel, $L_2$Ni(bt) and $L_2$Ni(dbt) [$L_2$ = $(CO)_2$, $(PH_3)_2$, $(NH_3)_2$, acac$^-$,† $(Cl^-)_2$, $(CN^-)_2$] to form hydrogen bonds with complementary probe molecules has been studied using density functional molecular orbital theory. The charge on the *trans* ligands, L, is found to be the dominant factor in determining the strength of the hydrogen bonding. The π donor and acceptor properties of the ligands are relatively unimportant. Increasing the negative charge on the ligands enhances hydrogen bonding in biureto complexes, where there is an excess of proton acceptor groups. In dithiobiureto complexes, where proton donor groups are in excess, the influence of the *trans* ligands is much smaller, and in the opposite direction; greater negative charge reducing the strength of the hydrogen bonds. These results suggest an approximately two-fold greater susceptibility of the proton acceptor groups to changes at the metal centre.**

## Introduction

The importance of hydrogen bonding in supramolecular chemistry and molecular recognition is well established.[1] The directional nature of the hydrogen bond permits the rational design of co-crystals from components displaying complementary sequences of hydrogen bonding sites. The significance of these complementary interactions in the pairing of DNA bases has been recognised for some time, but the phenomenon is far more widespread, and may be responsible for the recognition of a wide variety of biologically significant molecules.[2] The majority of work in this field has centred on the synthesis of co-crystals of purely organic molecules, resulting in the design of novel liquid crystal polymers,[3] supermolecular mesophases[4] and materials with non-linear optical properties.[5] Within this laboratory, interest has centred on the extension of these principles to complexes incorporating transition metal ions.[6] This relatively recent development presents the possibility of altering the nature of the hydrogen bonded network *via* changes at the metal centre. In addition, the introduction of paramagnetic metal ions and transition metal chromophores into the system may lead to extended structures with interesting magnetic and electronic properties. Several ligands have now been developed which exhibit hydrogen bonding sites in addition to the coordinating groups, and co-crystals between complexes of these ligands and a variety of complementary organic molecules have been structurally characterised.[7]

In the absence of relevant experimental and theoretical work, the role of the transition metal ion in the three-dimensional network is unclear. It may simply act as a template, dictating the orientation of the remote hydrogen bonding surfaces as a consequence of the stereochemical preferences of the ion. Alternatively, the metal may exert a specific electronic influence on the groups at the remote hydrogen bonding site, thereby providing a means of tuning the strength of the intermolecular interactions. In this paper, we aim to distinguish between these two possibilities with the aid of molecular orbital theory calculations on model systems.

The utility of density functional theory (DFT) as a tool for studying the electronic structure of transition metal complexes is well established,[8] its primary advantages over conventional *ab initio* techniques being the economy with which electron correlation can be incorporated into the calculation. More recently, gradient corrected DFT has been shown to provide an excellent description of weaker interactions such as hydrogen bonds,[9] where correlation also makes a significant contribution to the total energy. In a previous paper we assessed the reliability of the DFT in organic supermolecular systems containing hydrogen bonds.[9d] In this paper we tackle for the first time the implications of introducing transition metal ions into the hydrogen bonded network. Specifically, we use DFT to calculate the hydrogen bond energies between a variety of square-planar nickel complexes of biuret (bt) and dithiobiuret (dbt) (Fig. 1) and complementary probe molecules (melamine and cyanuric acid respectively). Both ligands present a triplet of hydrogen bonding sites to a receptor molecule, but in the former there is an excess of proton acceptor (A) sites, while the latter exhibits an excess of proton donor sites (D). The different response of the two ligands to changes at the metal centre allows us to draw conclusions regarding the relative susceptibilities of proton donor and acceptor sites to changes at the metal centre, and consequently to postulate design principles aimed at optimising hydrogen bonding in co-crystals.

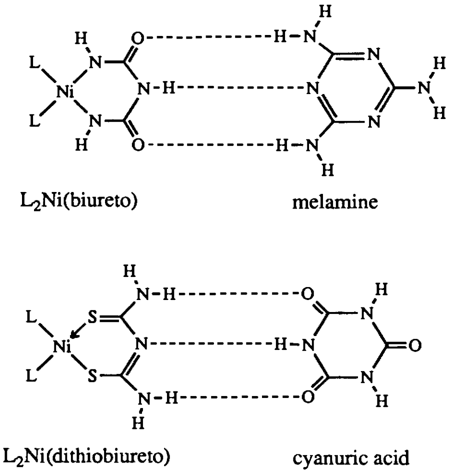

**Fig. 1** Molecular structure of $L_2$Ni(bt)·melamine (bt = biuret) and $L_2$Ni(dbt)·cyanuric acid (dbt = dithiobiuret) pairs

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† Throughout this paper the propanedialato ligand, $C_3O_2H_3^-$, is used to model acetylacetonate, acac$^-$.

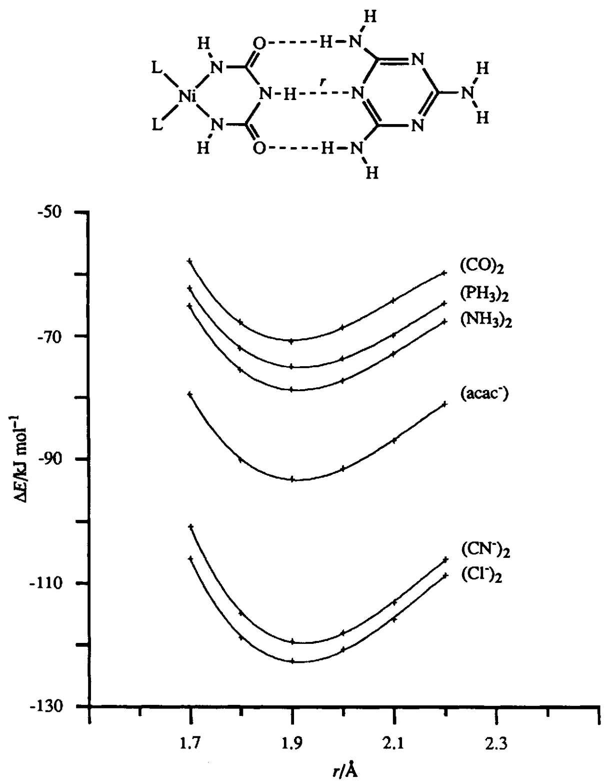

**Fig. 2** Interaction energies for complexes of biuret with melamine

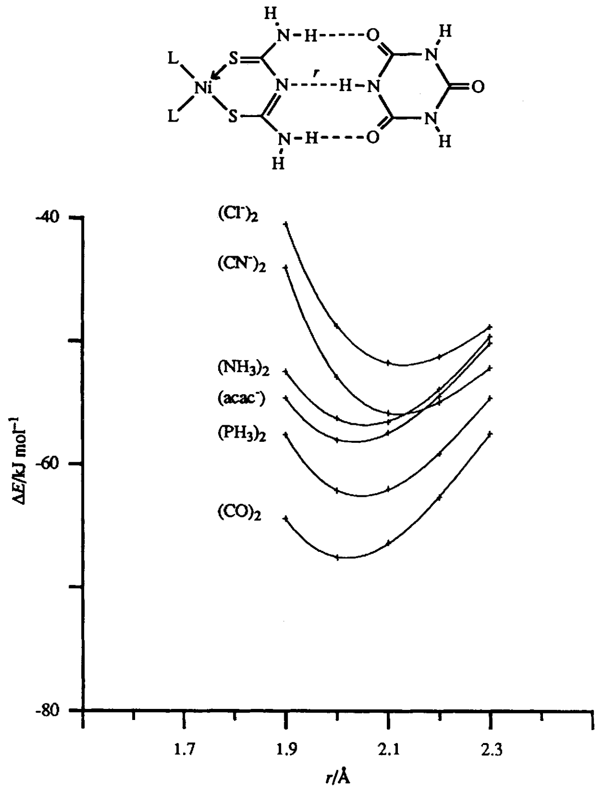

**Fig. 3** Interaction energies for complexes of dithiobiuret with cyanuric acid

## Computational methods

All calculations were performed using the Amsterdam Density Functional Package[10] of Baerends and co-workers. A basis set of triple-ζ quality was used for the Ni ($3d^9 4s^1$), and of double-ζ quality for main group atoms C, N, O, P, S, Cl and H.[11] The bases for C, N, O, P, S and Cl were augmented with a single d polarisation function, while a single p function was employed for H. Core orbitals (1s,2s,2p,3s,3p for Ni, 1s for C, N, O and 1s,2s,2p for P, S, Cl) were frozen.[12] An auxiliary set of s,p,d,f and g Slater type orbitals was used to fit the molecular density. The geometries of the component monomers were optimised within the local density approximation (LDA) in the parameterisation of Vosko, Wilk and Nusair,[13] using analytical gradient techniques.[14] The hydrogen bond energies were then computed using the generalised transition state approximation of Ziegler *et. al.*,[15] using the self-consistent orbitals of each component monomer as a basis for the supermolecular calculation. The gradient corrections to exchange (Becke)[16] and correlation (Perdew)[17] were incorporated as a perturbation in the final fragment calculation. The neglect of geometric relaxation of the two components in the complex has been shown to have only a minor influence on the calculated interaction energies.[9d]

## Results and discussion

In Figs. 2 and 3, total interaction energies for square planar nickel complexes of bt and dbt with melamine and cyanuric acid respectively, are shown as a function of the central hydrogen bond distance, $r$. The optimised hydrogen bonded distances are relatively insensitive to the identity of the ligand, values of $r$ lying at approximately 1.90 and 2.10 Å for bt and dbt complexes respectively. No crystallographic data are available for bt complexes hydrogen bonded to an appropriate receptor, but the optimised values of approximately 1.90 Å are typical of calculated values for purely organic systems exhibiting a triplet of hydrogen bonds.[18] The larger calculated distances in the dbt complexes are consistent with the crystallographic data available from the structures of Ni(dbt)$_2$·uracil,[7a] Ni(dbt)$_2$·bemegride[7b] and Ni(dbt)$_2$·1,8-naphthalimide,‡[7b] where the central hydrogen bond distances are in the vicinity of 2.10 Å. The unusually long central hydrogen bond arises as a consequence of the structural requirements of the coordinated dbt ligand, which are somewhat different to those of bt due to the presence of sulfur at the coordination sites. The long Ni–S bonds (*ca.* 2.10 Å) and large S–Ni–S bite angle (*ca.* 100°) combine to force the $NH_2$ proton donor groups towards the docking site, as a consequence of which the two external hydrogen bonds are between 0.2 and 0.3 Å shorter than the central hydrogen bond in all cases. The long central hydrogen bond therefore represents the best compromise between the optimum requirements of the central and external hydrogen bonds.

The calculations summarised in the two figures demonstrate that the strength of the hydrogen bonding is indeed influenced by the ligands attached to the metal, the most significant factor being the overall charge on the complex. Neutral bt complexes [$L_2$ = $(CO)_2$, $(PH_3)_2$ and $(NH_3)_2$] have association energies in the region 70–80 kJ mol$^{-1}$, while increasing the negative charge on the metal complex leads to a significant enhancement in the hydrogen bonding, dianionic systems [$L_2 = (Cl^-)_2, (CN^-)_2$] having association energies approximately 50 kJ mol$^{-1}$ greater than their neutral counterparts. Within a subgroup of complexes of the same charge, the electronic properties of the ligand exert a relatively minor influence, as illustrated by the very similar interaction energies of $Cl^-$ and $CN^-$ complexes (π donor *vs.* π acceptor respectively) and of CO and $NH_3$ complexes (σ donor/π acceptor *vs.* σ donor only).

Interaction energies for dbt complexes (Fig. 3) are again determined predominantly by the overall charge on the metal complex, but in this case optimum hydrogen bonding is obtained with the neutral ligands, increased negative charge leading to reduction in interaction energy. In addition, the

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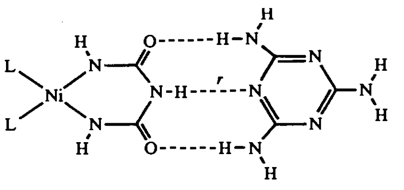
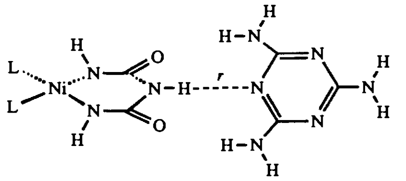
‡ Bemegride = 4-ethyl-4-methylpiperidine-2,6-dione; 1,8-naphthalimide = naphthalene-1,8-dicarboximide.



Parallel ( ∥ ) Conformation



Perpendicular ( ⊥ ) Conformation

**Fig. 4** Parallel and perpendicular orientations of the two components of a molecular pair

**Table 1** Net charges on $L_2Ni$ and bt or dbt fragments

| | $L_2$ | $q(L_2Ni)$ | $q$(bt/dbt) |
|---|---|---|---|
| $L_2Ni$(bt) | $(CO)_2$ | +0.515 | −0.515 |
| | $(PH_3)_2$ | +0.695 | −0.695 |
| | $(NH_3)_2$ | +0.868 | −0.868 |
| | $(acac^-)$ | −0.058 | −0.942 |
| | $(CN^-)_2$ | −0.939 | −1.061 |
| | $(Cl^-)_2$ | −0.873 | −1.127 |
| $L_2Ni$(dbt) | $(CO)_2$ | +0.479 | +0.521 |
| | $(PH_3)_2$ | +0.752 | +0.248 |
| | $(NH_3)_2$ | +0.795 | +0.205 |
| | $(acac^-)$ | −0.024 | +0.024 |
| | $(CN^-)_2$ | −0.819 | −0.181 |
| | $(Cl^-)_2$ | −0.741 | −0.259 |

**Table 2** Interaction energies (kJ $mol^{-1}$) for bt and dbt complexes in parallel (∥) and perpendicular (⊥) conformations

| | $L_2$ | ∥ | ⊥ | ∥ − ⊥ |
|---|---|---|---|---|
| $L_2Ni$(bt) melamine | $(CO)_2$ | −16.92 | −6.04 | −10.88 |
| | $(PH_3)_2$ | −17.90 | −4.46 | −13.24 |
| | $(NH_3)_2$ | −18.79 | −3.82 | −14.97 |
| ($r$ = 1.90 Å) | $(acac^-)$ | −22.26 | −2.32 | −19.94 |
| | $(CN^-)_2$ | −28.52 | −2.18 | −26.34 |
| | $(Cl^-)_2$ | −29.27 | −2.35 | −26.92 |
| $L_2Ni$(dbt) cyanuric acid | $(CO)_2$ | −15.86 | −0.41 | −15.45 |
| | $(PH_3)_2$ | −14.82 | −1.33 | −13.49 |
| | $(NH_3)_2$ | −13.53 | −1.51 | −12.02 |
| ($r$ = 2.10 Å) | $(acac^-)$ | −13.73 | −4.53 | −9.20 |
| | $(CN^-)_2$ | −12.37 | −6.91 | −5.46 |
| | $(Cl^-)_2$ | −12.79 | −7.86 | −5.49 |

influence of the different ligands is much less than in the series of bt complexes, the interaction energies spanning a range of only 20 kJ $mol^{-1}$. The energies for complexes of dbt are also uniformly lower than their bt counterparts, probably because of the disparity between central and external hydrogen bond lengths, which means that at the equilibrium separation of 2.1 Å, neither central nor external hydrogen bonding is maximised.

The gross trends summarised in Figs. 2 and 3, *viz* optimal hydrogen bonding for negatively charged complexes of bt and neutral complexes of dbt, are readily interpreted in terms of the transfer of charge from the $L_2Ni$ moiety to the hydrogen bonding ligand. Net atomic charges for the $L_2Ni$ and bt/dbt fragments are summarised in Table 1, from which it is clear that the charge on the bt or dbt ligands is strongly dependent upon that on the ligands in the *trans* positions. As the net negative charge on the bt or dbt ligands increases, so too will the ability of the proton acceptor sites to form hydrogen bonds, while the proton donor sites will show an affinity for potential proton acceptors. Thus in complexes of bt, where proton acceptor sites are in excess, the gross trend is towards stronger bonding in negatively charged complexes. Conversely in the dbt complexes, where proton donor sites predominate, optimal hydrogen bonding is found in neutral complexes.

Whilst this simple consideration of the number of donor and acceptor sites can explain the direction of the observed trends, it cannot account for the notably greater sensitivity of bt complexes to changes at the metal centre. This latter observation suggests that the two types of hydrogen bonding sites are not equally susceptible to changes at the metal centre, and hence we must consider the changes occurring at proton and acceptor sites in isolation. To a first approximation, the total hydrogen bonding energy may be expressed as the sum of the three individual interactions, one unique central bond and two symmetry-related external bonds. In order to delineate the relative contributions of these two distinct types of hydrogen bonds to the overall stability of the complex, an additional series of calculations was performed in which the two molecular fragments were mutually rotated by 90°, as shown in Fig. 4. The total interaction energy in this perpendicular (⊥) conformation represents the contribution of the central hydrogen bond in isolation, while the difference between the interaction energy in the perpendicular conformation and that in the original parallel (∥) arrangement may be identified with the contribution of the two external bonds in isolation. In order to aid a systematic comparison, all calculations in the ⊥ orientation were performed at $r$ = 1.90 Å for bt complexes and at $r$ = 2.1 Å for those of dbt. Calculated interaction energies in both ⊥ and ∥ orientations, along with the difference, (∥ − ⊥), are summarised in Table 2.

In the bt complexes, the central hydrogen bonding site is a proton donor, while the two external sites are both proton acceptors. On replacing two CO ligands with two $Cl^-$ ions, the hydrogen bonding in the ⊥ conformation is decreased by less than 4 kJ $mol^{-1}$, while the (∥ − ⊥) term increases by over 16 kJ $mol^{-1}$. These results are in accord with the qualitative expectation that electron donor ligands should enhance the capacity of the proton acceptor sites to hydrogen bond, but diminish the ability of the N–H group to act as a proton donor. The magnitude of the changes also indicates that proton acceptor sites are approximately twice§ as sensitive as proton donors to changes at the metal centre. Thus the enhanced hydrogen bonding at the external proton acceptors greatly outweighs the relatively minor reduction in hydrogen bonding at the central proton donor, resulting in a net increase in interaction energy as the negative charge is increased.

In the dbt complexes, the central site is a proton acceptor, while the external sites are proton donors, and Table 2 again indicates that the sensitivity of the proton acceptor (⊥ conformation) is approximately double that of the proton donors. Increasing the electron density at the Ni centre causes a relatively small decrease in hydrogen bonding capacity at the two external proton donor sites, which is almost entirely offset by the large decrease in bonding at the single central proton acceptor site. The net result is that the dbt complexes are far less sensitive to the ligand environment than are their bt counterparts.

The greater range of interaction energies associated with proton acceptor sites can be rationalised by considering the canonical forms of the two coordinated ligands, illustrated in Scheme 1. In both bt and dbt complexes, the generation of a negative charge at the proton acceptor sites is accompanied by

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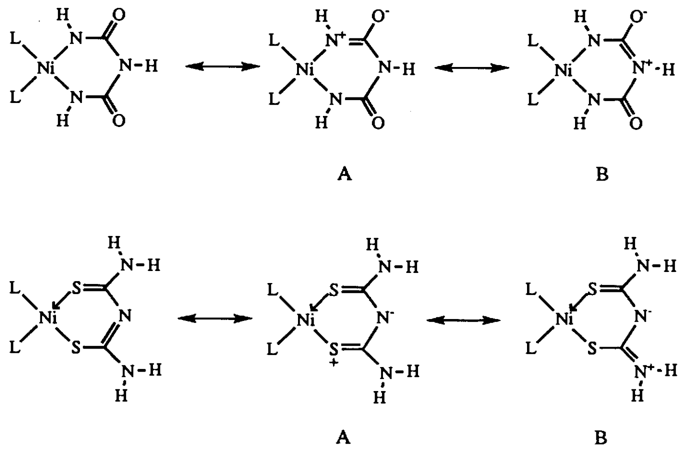
§ The term (∥ − ⊥) accounts for the effects of two identical interactions.



**Scheme 1** Canonical forms of biureto- and dithiobiureto-complexes

the development of a positive charge at the ligand atom adjacent to the metal (canonical forms A). In contrast, the canonical forms in which a positive charge is generated at the proton donor sites result in a negative charge at atoms remote from the metal centre (canonical forms B). The ligands attached to the metal ion in the *trans* positions are therefore much less able to exert a direct influence on the electron density at the proton donor sites. In addition, the positive charge at the proton donor site arises at the nitrogen atom, whereas it is the proton itself which accepts electron density when a hydrogen bond is formed. Changes in the charge on the nitrogen atom can only be communicated to the proton *via* the N–H $\sigma$-bond in an inductive pathway, and the proton is therefore further buffered from the influence of the metal ion. Thus the combination of unfavourable conjugative and inductive effects renders the proton donor sites far less sensitive to the effects of the metal ion than the proton acceptor sites.

## Conclusion

In this paper we have assessed the hydrogen-bonding capability of square-planar nickel complexes of biuret and dithiobiuret in the presence of a variety of different *trans* ligands. This is the first time that such a study has been made on a hydrogen bonding system containing metal ions. The calculations have shown that the metal ion does indeed influence the strength of the hydrogen bonding interactions. The principle factor in determining the strength of the interaction is found to be the net charge on the *trans* ligands coordinated to the metal. Other features such as the $\pi$ donor or $\pi$ acceptor properties of the ligand are of secondary importance.

An increase in the negative charge on the complex enhances the ability of proton acceptor groups to form hydrogen bonds, but has the opposite effect on proton donors. In bt complexes, where the proton acceptors outnumber the donors, the net effect of increasing the electron density is to enhance the hydrogen bonding. The converse is true in dbt complexes, where the proton donor groups are in excess, and increasing the electron density at the metal reduces the hydrogen bonding capacity. The magnitude of the changes within a series are, however, rather different, dbt complexes being far less susceptible to changes in the coordination environment of the metal than those of bt.

By rotating one component of a molecular pair by 90°, it is possible to isolate the central hydrogen bond, and thereby separate the contributions of proton donors and proton acceptors to the total stability of an individual complex. The susceptibility of the proton donor groups to changes at the metal centre is found to be approximately half that of the proton acceptors. As a consequence, changes at the two proton donor sites in dbt are almost offset by those at the single proton acceptor site. In bt complexes, the more susceptible proton acceptor groups are in excess, resulting in a much greater response of the complex as a whole to changes in the charge density at the nickel atom.

The work described here forms part of a concerted effort within this laboratory to optimise hydrogen bonding in systems containing metal ions, and hence to synthesise new crystalline materials based on three-dimensional hydrogen bonded networks containing transition metal ions. In light of the theoretical results described above, we can propose several design principles aimed at optimising the intermolecular interactions. Firstly, the structural properties of the ligand and spacer molecule must be compatible in the sense that all acceptor–donor distances should be approximately equivalent, any significant asymmetry in the hydrogen bonds necessarily leading to less than optimal hydrogen bonding. Secondly, the greater susceptibility of proton acceptor groups to the influence of the metal group suggests that the greatest scope for tuning hydrogen bonds will occur in complexes where the coordinated ligand has an excess of acceptor groups (ADA as in bt), rather than of donors (DAD as in dbt). Finally, within a series of complexes, the net charge on the complex has the strongest influence, indicating that negatively charged complexes of ADA type ligands will provide the optimal conditions for strong hydrogen bonding.

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