

Hydrogen Bonding in Organometallic Crystals. 3.¹ Transition-Metal Complexes Containing Amido Groups

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Intermolecular hydrogen bond distribution and geometry in crystals of transition-metal complexes containing primary and secondary amido groups have been investigated by searching the Cambridge Structural Database (CSD). The hydrogen-bonding patterns have been compared with those observed in crystalline organic amides. Organometallic systems show a great structural variability as well as the participation in the hydrogen-bonding patterns of other donor/acceptor systems such as ligated or solvent water molecules. The effect of the coordination via the amide O-atoms to the metal centers on the hydrogen-bonding capacity has been examined as well as the participation of CO ligands. The hydrogen bonding parameter distribution has been analyzed also in the case of ionic species and compared to the neutral crystals. It has been shown that hydrogen bond interactions in organometallic amido complexes are generally longer than in pure organics, though this is compensated by the formation of a greater number of bonds per molecule because of the more frequent occurrence of bifurcation. Some selected crystal structures have been examined in detail, especially with respect to very short NH...O contacts.

Introduction

Hydrogen bonding is the major cohesive force in many molecular crystals of the organic, organometallic and inorganic type.² It is well-known that this interaction plays a major role in determining the conformation of nucleic acids, proteins, and polysaccharides. Hydrogen bonding is the master key to molecular recognition,³ and a thorough understanding of this phenomenon is indispensable in the field of crystal engineering, which is in actuality solid-state molecular recognition.⁴ Crystal engineering enables the design of solid materials with predefined physical and chemical properties.

In spite of the large number of studies devoted to hydrogen bonding, many aspects of this subject are still unexplored. For example, we have recently begun to appreciate the importance of these interactions in organometallic systems.⁵ As we proceed with the investigation of hydrogen bond patterns in organome-

tallic crystals and compare our observations with the large body of information accumulated for organic systems, it is becoming apparent that organometallic molecules share many but not all characteristics of the pure organic molecules. For example, transition-metal carbonyl complexes and clusters, which present a large number of CO ligands coordinated in various bonding modes, have been shown to be particularly prone to formation of intermolecular CH...O bonds in which the carbonyl oxygen is the hydrogen-bonding acceptor.⁶ These interactions, though weaker than those established between carboxylic or hydroxylic groups, are important because of the large number of acceptors and donor groups that are usually present even in simple coordination complexes or organometallic molecules.

Differences between organic systems on the one hand and organometallic systems on the other arise from the interaction of the organic molecules (the ligands) with the metal center or centers. The metal-ligand bonding influences the patterns of hydrogen bonds that can be established, although the variability is great and generalizations are to be taken with caution. The effect of the coordination to the metal(s) is essentially twofold. On the one hand, one must consider the electronic effects of donation/back-donation in bonding established by many organic fragments (arenes, cyclopentadienyl ligands, alkynes, alkenes, etc.) as well as in the direct M-X σ -bonding (X = C, N, O, etc.), which affects the polarity of C-H, N-H, and O-H bonds and therefore the acidity of the hydrogen atoms. On the other hand,

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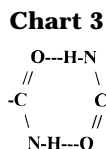
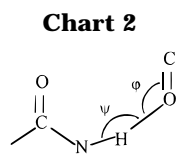
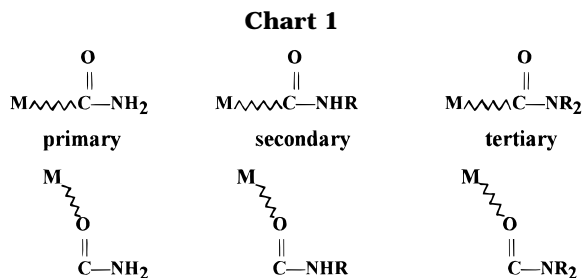
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there is the definite possibility that hydrogen-bond acceptor atoms can be used alternatively in the complexation *via* lone-pair donation to empty orbitals on the metal atoms.

In this paper we report the results of our study of the hydrogen-bonding patterns in transition-metal amido complexes, hereinafter referred to as OM complexes.⁷ This group includes complexes in which primary and secondary amido groups are either directly linked to the transitional metal center(s) or belong to a larger metal-coordinated ligand system (see Chart 1).

Before proceeding with the discussion, it is worth recalling the key aspects of the hydrogen bond between amides in organic crystals.⁸ In primary amides the CO-NH₂ group is planar and the maximum electrostatic strength of the intermolecular hydrogen bond is achieved when the N-H vector is collinear with the lone pairs of the oxygen atoms. When the O atom belongs to a C=O fragment, the H---O=C angle (φ in Chart 2) is therefore generally around 120–140°, though angles close to 180° are not uncommon. The N-H---O angle (ψ in Chart 2) tends toward linearity. No hydrogen bonds of the type NH---N are observed in organic amide crystals. In general, organic amides form hydrogen-bonded dimers of the type shown in Chart 3, similar to those observed for organic carboxylic acids, although donor–acceptor N---O distances in amides span a much wider range than O---O hydrogen-bonded distances in carboxylic acids. Relevant exceptions are the tetragonal and rhombohedral forms of acetamide as well as adipamide, chloroacetamide, azodicarbonamide, and nicotinamide, in which hydrogen-bonded pairs are not formed.^{8a} The second proton (obviously absent in carboxylic acids) in the centrosymmetric pair forms an additional hydrogen bond to an oxygen of a second amide pair.

It is worth recalling here that the hydrogen bonding in amides has also been approached theoretically. Much

of the early work on potential energy treatments has been summarized in a paper by Dauber and Hagler.⁹ The most recent attempt to treat hydrogen bonds in molecular crystals *via* potential energy approach is that of Gavezzotti and Filippini.¹⁰ In this latter study, 24 primary and 55 secondary amides were investigated. The average geometrical parameters showed no appreciable difference between structural parameters in primary and secondary amide crystals, although the average N---O distance is slightly longer in the former (2.95(6) versus 2.90(7) Å). The role of Coulombic forces in the crystal packing of amides has been investigated from atomic multipole moments derived from low-temperature X-ray diffraction data for acetamide and formamide,¹¹ while lattice energy minimization procedures have been used to study the packing of adipamide.¹²

Amides are of interest in studies of intermolecular interactions in organometallic systems not only because the two amido H-atoms in primary amides usually form geometrically, and perhaps energetically, distinct interactions but also because of the definite possibility for the amide to act as a ligand by coordinating to metal centers *via* the O-atom lone pairs. This type of interaction (see Chart 1), obviously not possible in organic amides, brings one of the hydrogen atoms close to the metal center, thus precluding the participation of this H atom in hydrogen bond formation. A second aspect of some importance is related to the competition of other acceptor groups with the amide O-atom in the formation of H-bonds. We have shown previously that the carbonyl ligand, for example, can compete with moderate acceptors, such as the hydroxyl group, and that it is also systematically involved in CH---O bonds.^{1,5}

In this paper we will address the following questions. (i) Do amide groups behave in the same way in organic and organometallic crystals with regard to their hydrogen-bond forming ability? (ii) Is there any difference in H-bonding patterns formed by primary and secondary amides? (iii) What is the effect on the hydrogen-bonding pattern of the coordination to the metal center of the amide oxygen atoms? (iv) Is the CO ligand (when present) capable of competing with the amide oxygen in terms of hydrogen-bonding acceptor capacity?

In order to address these questions, we have searched the Cambridge Structural Database (CSD)¹³ for coordination complexes containing amido groups. Some selected crystal structures have been examined in greater detail, with particular attention to very short NH---O contacts.

Experimental Section

Cambridge Structural Database (CSD) Analysis. Data were retrieved from the October 1994 update version (5.05) of the CSD (109 816 entries) for all crystal structures with an exact match between chemical and crystallographic connectivity.¹³ Both neutral and charged species were considered. Only entries where $R < 0.10$ and where atomic coordinates are given were considered. Primary and secondary amido groups were retrieved separately for organic and OM complexes. Geo-

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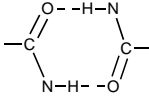
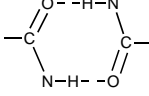
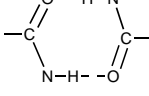
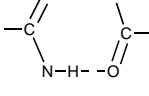
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Table 1. Mean Geometrical Parameters for NH---O Hydrogen Bonds in Organometallic Complexes Containing Primary and Secondary Amido Groups and in Organic Amides^a

set type	fragment	H---O (Å)	N---O (Å)	no. of contacts	unique REFCODES	N-H---O (deg)
Primary Amido Groups—OM Complexes						
A	O=C—N—H---O	2.21(1)	3.09(1)	369	95	148.8(9)
B	O=C—N—H---O=C	2.14(2)	3.03(1)	120	66	152.9(16)
C	O=C—N—H---O=C—N—H	2.15(3)	3.04(2)	77	49	150.9(22)
D		2.07(3)	2.99(1)	38	35	157.1(28)
		2.07(3)	3.00(2)			158.1(28)
Primary Amides—Organic Species						
A	O=C—N—H---O	2.10(1)	3.02(1)	1014	432	155.9(5)
B	O=C—N—H---O=C	2.04(1)	2.98(1)	709	375	158.5(5)
C	O=C—N—H---O=C—N—H	2.03(1)	2.97(1)	513	308	159.8(7)
D		1.97(1)	2.95(1)	192	181	167.3(8)
		1.97(1)	2.95(1)			167.3(8)
Secondary Amido Groups—OM Complexes						
A	O=C—N—H---O	2.10(2)	3.00(1)	451	220	153.2(8)
B	O=C—N—H---O=C	2.03(2)	2.96(2)	151	96	151.0(12)
C	O=C—N—H---O=C—N—H	2.02(2)	2.96(2)	112	69	159.0(13)
D		1.89(2)	2.89(2)	56	45	168.1(11)
		1.90(2)	2.89(2)			167.5(11)
Secondary Amides—Organic Species						
A	O=C—N—H---O	2.01(1)	2.95(1)	3974	2659	158.6(3)
B	O=C—N—H---O=C	1.99(1)	2.94(1)	3026	2125	159.6(4)
C	O=C—N—H---O=C—N—H	1.98(1)	2.93(5)	2422	1724	160.5(4)
D		1.90(1)	2.87(1)	664	593	166.3(6)
		1.91(1)	2.88(1)			166.5(6)

^a Standard deviations are given in parentheses.

metrical calculations were performed on these amide subsets for NH---O hydrogen bonds with H---O distances between 1.40 and 2.80 Å and N—H---O, that is, ψ angles, between 110 and 180°. H-atom positions were invariably normalized to the neutron values (C—H 1.08 Å; N—H 1.01 Å; O—H, 0.98 Å). Duplicate hits (identified by the same REFCODES) were manually removed by eliminating the structure with the highest *R* value in each case. Key examples were selected from the search outputs and were investigated by computer graphics.^{14a} The computer program PLATON^{14b} was used to analyze the metrical features of the hydrogen-bonding patterns. For other details of the CSD procedures, the reader is referred to earlier publications in this series.^{1,5}

Results and Discussion

For the sake of a consistent description and comparison between organic and OM systems, NH---O hydrogen bonds were classified into four categories according to changes in the acceptor moiety. The first set (A) contains all NH---O hydrogen bonds formed by amide protons with all possible acceptor O-atoms (carbonyl O, ether O, water, *etc.*), the second set (B) contains hydrogen bonds formed by only keto, amide, and ester carbonyl groups, and the third group (C) contains bonds formed by only amide carbonyl groups. Thus, the third group is a subset of the second, which is a subset of the first. The fourth group (D) is likewise a subset of the third and contains cyclic bonds of the type described in Chart 3. The results are summarized in Table 1.

With respect to the data collected in Table 1, one can observe that only 52% of the OM primary amides (49

out of 95) form the inter-amide bond NH---O in category C, whereas such bonds are present in as many as 71% of the organic primary amides (308 out of 432). Similarly, only 30% of the OM secondary amides (69 out of 220) form the NH---O bonds of category C, while as many as 65% of the pure organic secondary amides (1724 out of 2659) form this type of hydrogen bond. The participation of water (either as solvent or as ligand in the OM complex) in intermolecular hydrogen bonds does not affect the inter-amide hydrogen-bonding patterns. Water is found in 27 primary and 34 secondary OM amides, respectively.

It is evident that, for both organic and OM structures, category C hydrogen bonding is more frequent for primary rather than secondary amides, a factor which may be attributed to the greater number of amide H-atoms in the former group. Another fact worth noting is that the proportion of OM primary and secondary amides falling in category C (that is, O=C—NH---O=C—NH) is significantly less than for the organic amides. This difference not only is a consequence of the presence of other competing donors and acceptors, such as H₂O, NO₃⁻, *etc.*, with respect to organic amides but also reflects the existence of cases in which the amide O-atom is engaged in coordination to the metal center *via* one of its lone pairs. The behavior of primary and secondary amides as O-bound ligands has a twofold effect, since it decreases the number of acceptor sites available for hydrogen bonding and increases the steric hindrance around the oxygen atoms, which, in some cases, can altogether prevent inter-amide hydrogen-bonding formation.

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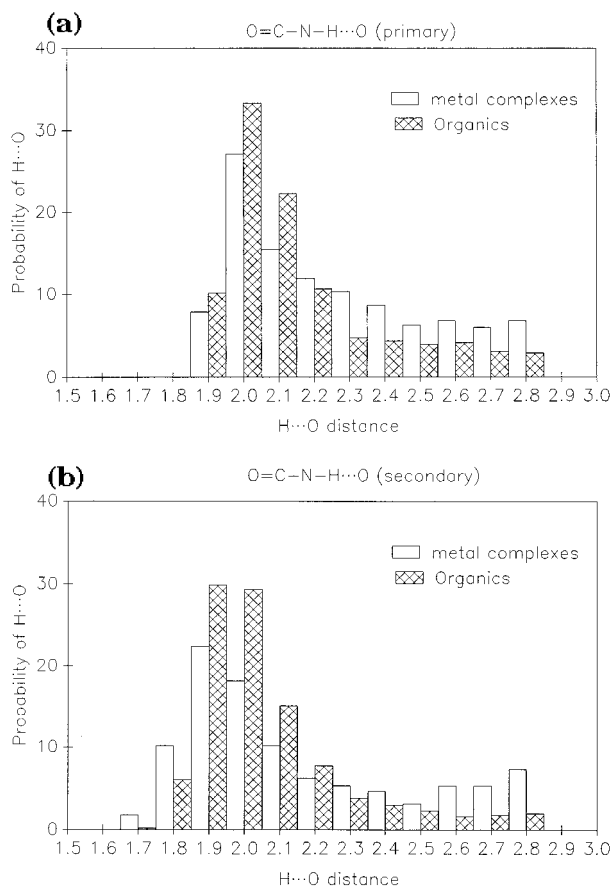


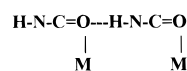
Figure 1. Distribution of the NH...O distances in organic (shaded columns) and OM crystals for (a) primary and (b) secondary amido groups.

We have analyzed this aspect with respect to the data grouped in the more general category A. Of the 95 primary and 220 secondary OM amido complexes in this category, 67 and 90 compounds, respectively, correspond to cases where the amide O-atom is bound to a transition metal. Of these, in a further subset of 33 and 23 cases, respectively, the O-atom is additionally bonded to an amide N-H group. The remainder, that is 34 and 67, may also be bonded but not to amide N-H groups. These hydrogen bonds are no different from the rest, and we conclude that ligation to a metal atom does not prevent an amide O-atom from accepting a hydrogen bond.

Of the 95 and 220 OM compounds containing primary and secondary amido groups, respectively, referred to above, 1 primary amide and 15 secondary amides contain the CO ligand and, of these, 7 of the latter category form NH...O hydrogen bonds to this CO ligand. Although these statistics are sparse, they are in general agreement with our earlier observations¹ concerning hard and soft hydrogen bonds. According to our suggestion, the hard donor N-H prefers hard acceptors such as amido CO groups, water, and so on, rather than the soft CO ligand acceptor.

Hydrogen Bond (NH...O) Distances. Histograms of the NH...O distances present in both organic and OM crystals are given for primary (Figure 1a) and secondary amides (Figure 1b). Both histograms show that the NH...O distribution for organic compounds is tighter than that for the OM compounds, for which there is a higher proportion of longer hydrogen bonds. For instance, while 33% and 27% of organic and OM hydrogen bonds occur in the peak range of 1.90–2.00 Å, this order

Chart 4



is reversed at longer separations: in the NH...O range 2.70–2.80 Å, one obtains 3% and 6% in the two respective categories. Again, from comparison between parts a and b of Figures 1, it can be noted that the lower limit of NH...O distances in secondary amides is somewhat shorter than for primary amides.

A steric factor may explain the presence of longer hydrogen bonds for OM compounds.¹⁵ However, this appears to be compensated by a larger number of bifurcated hydrogen bonds with respect to pure organic amides. This is borne out by the statistics on bifurcated hydrogen bonds: 39% of the hydrogen bonds in the primary amide OM compounds (144 out of 369) correspond to donor-bifurcated (or three-center) interactions. The percentage of bifurcated hydrogen bonds is only 25% in organic primary amides (252 out of 1014).¹⁶ A similar situation prevails for the secondary amides also. In general, these donor-bifurcated interactions are formed when the number of acceptors is greater than the number of donors.

In contrast to organic systems, many OM complexes are ionic. We have explored the effect of the ionic charge on the NH...O hydrogen bond lengths. It appears that the ionic charge does not cause any major change in the distribution of distances. No systematic shift of the NH...O distances can be detected in complexes carrying primary amido groups, while in the case of secondary amides there is a slight shift of the histogram maximum to greater values.

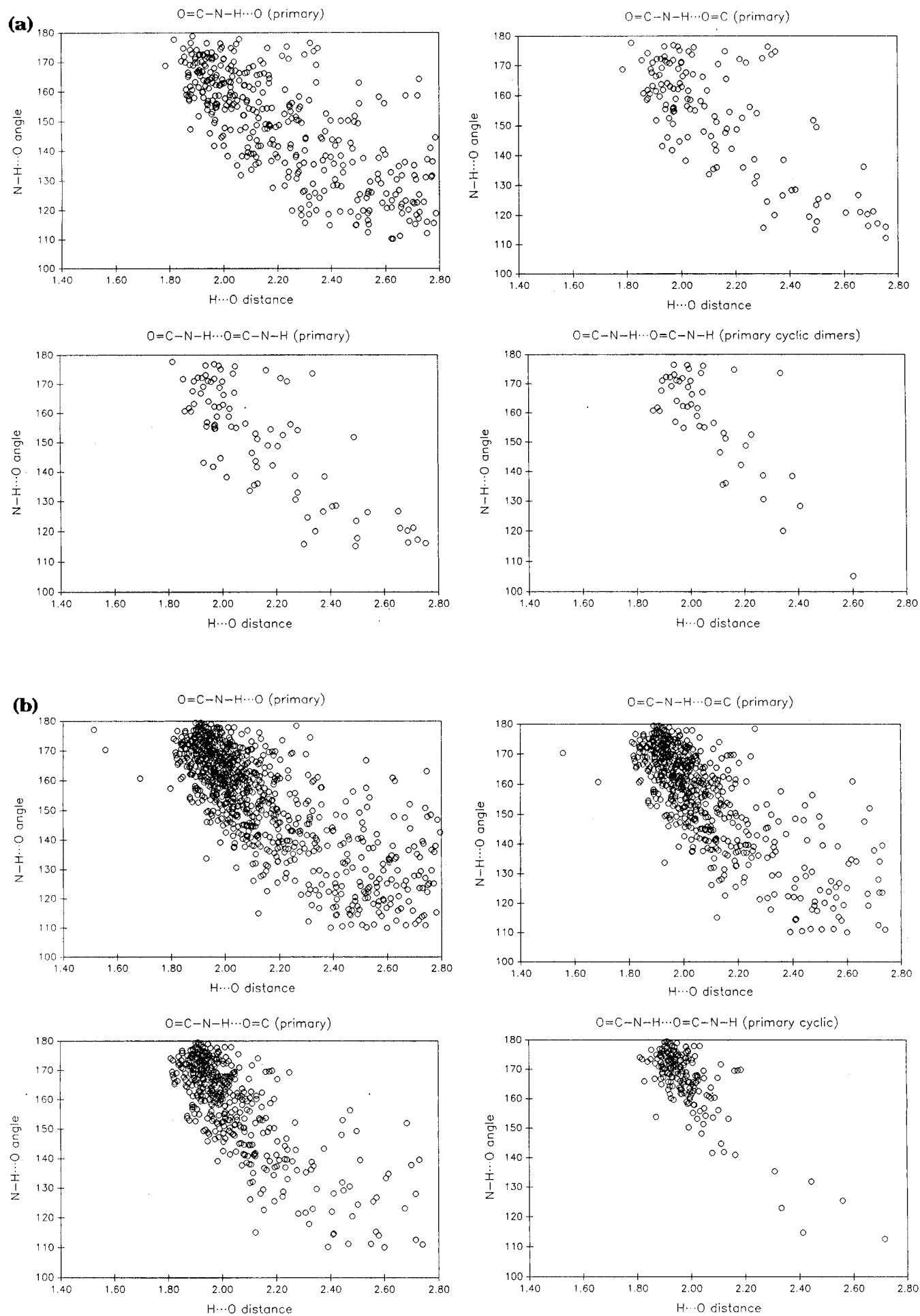
We have also looked at the distribution of NH...O distances of type C in the OM amides subset constructed with those crystal structures in which the amide O-atoms interact with the transition-metal atom of the complex (see Chart 4).

In the primary OM amido complexes there are 33 compounds for the above fragment; in the secondary OM amido complexes there are 23. Although the sample is not large enough to justify subtle comparisons, one can note that, while the lowest limit for NH...O interactions is 2.1 Å for primary and 2.0 Å for secondary OM amides, in keeping with the general trend, the limiting M-O bond distance is shorter for primary than for secondary OM amides (2.1 versus 2.2 Å). This difference arises from the greater steric hindrance of secondary amides with respect to primary amides, although electronic contributions cannot be confidently ruled out on the basis of pure statistics.

N-H...O Angles (ψ). Figure 2 shows scatterplots of the N-H...O (ψ) angles versus NH...O distances for primary OM amides. Each scatterplot is made up of four parts, one for each type of hydrogen bond subset described above. The general features are, however, extremely similar. In all cases the N-H...O angles span a rather ample range (120–180°), although there is a marked tendency to concentrate at higher angles

(15) A χ^2 analysis for the H...O distributions showed that they are deviating from normal distribution and that these deviations are larger in the long H...O domain (>2.5 Å). Percentage-wise this effect is more evident for OM than for organics.

(16) An interaction is accepted as bifurcated if there are at least two O-atoms within 2.80 Å of an amido H-atom such that both N-H...O angles lie in the range 110–180°. For a more detailed account of the criteria governing bifurcation, see: Parthasarthy, R. *Acta Crystallogr., Sect. B* **1969**, B25, 509.



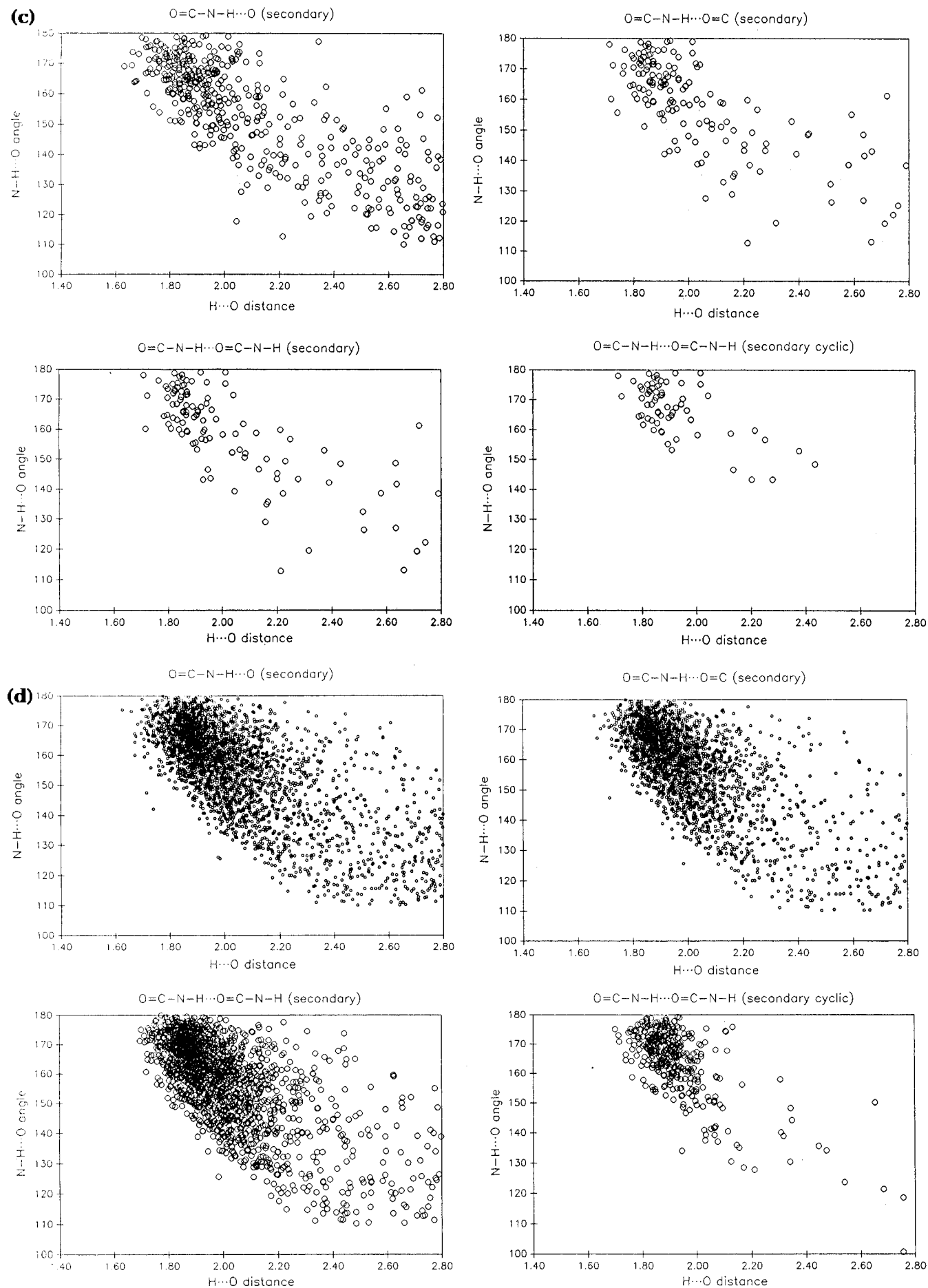
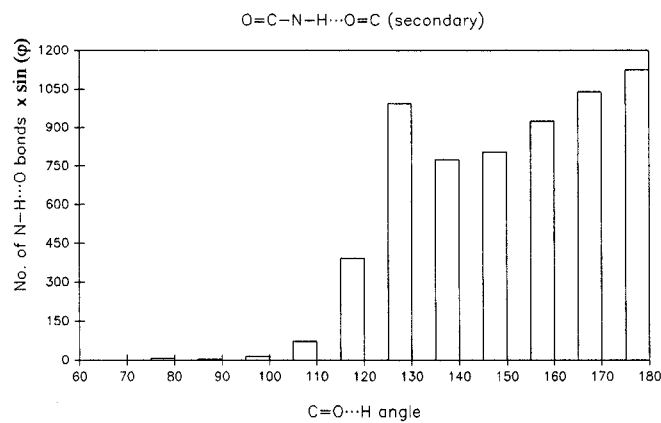
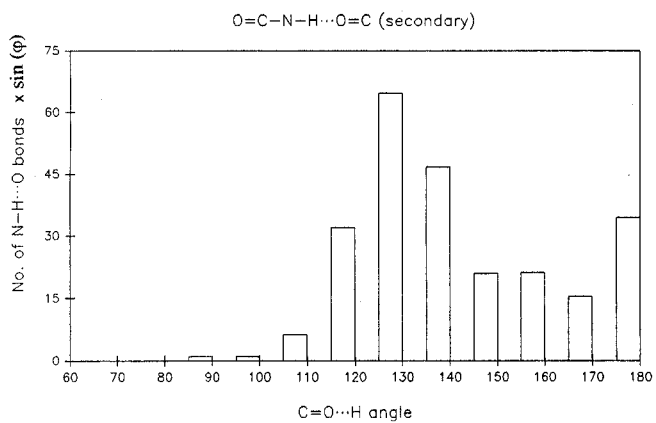
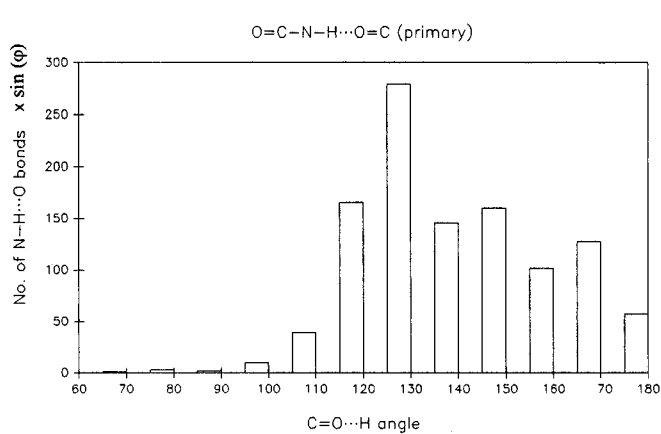
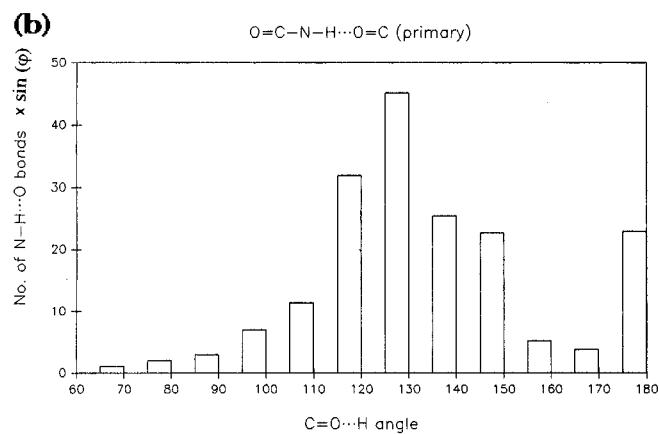
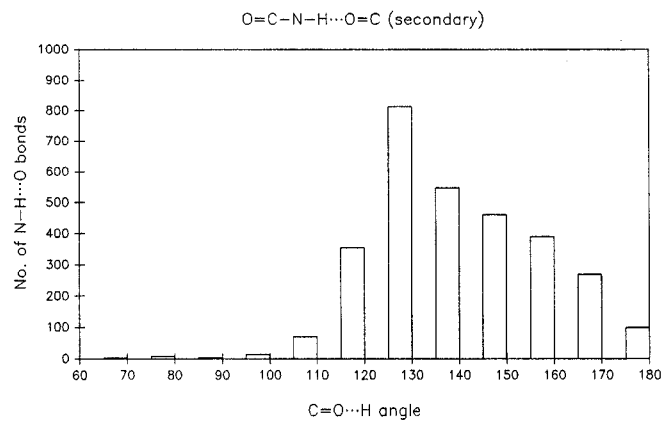
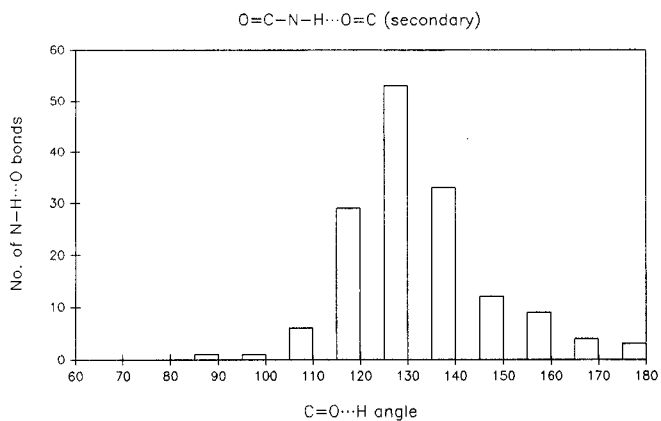
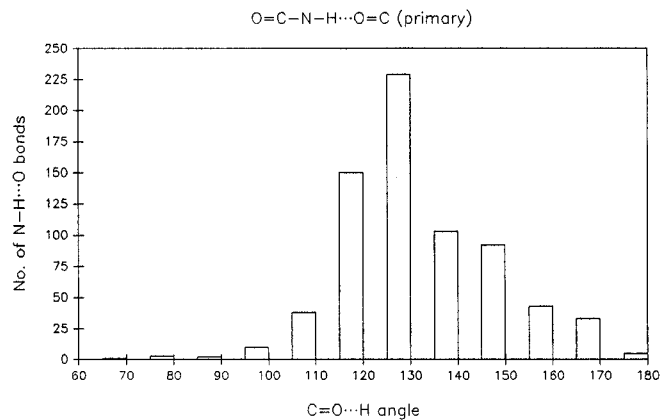
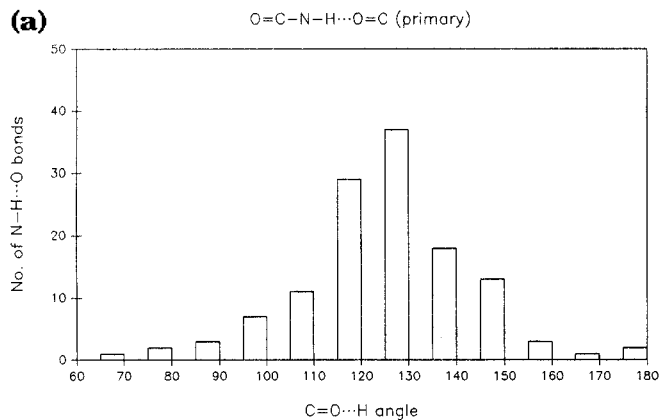


Figure 2. Scatterplots of N-H...O angles (deg) versus NH...O distances (Å): (a) primary OM amides; (b) primary organic amides; (c) secondary OM amides; (d) secondary organic amides. For all scattergrams the sequence is as follows: top left, bonds of type A; top right, B; bottom left C; bottom right, D.



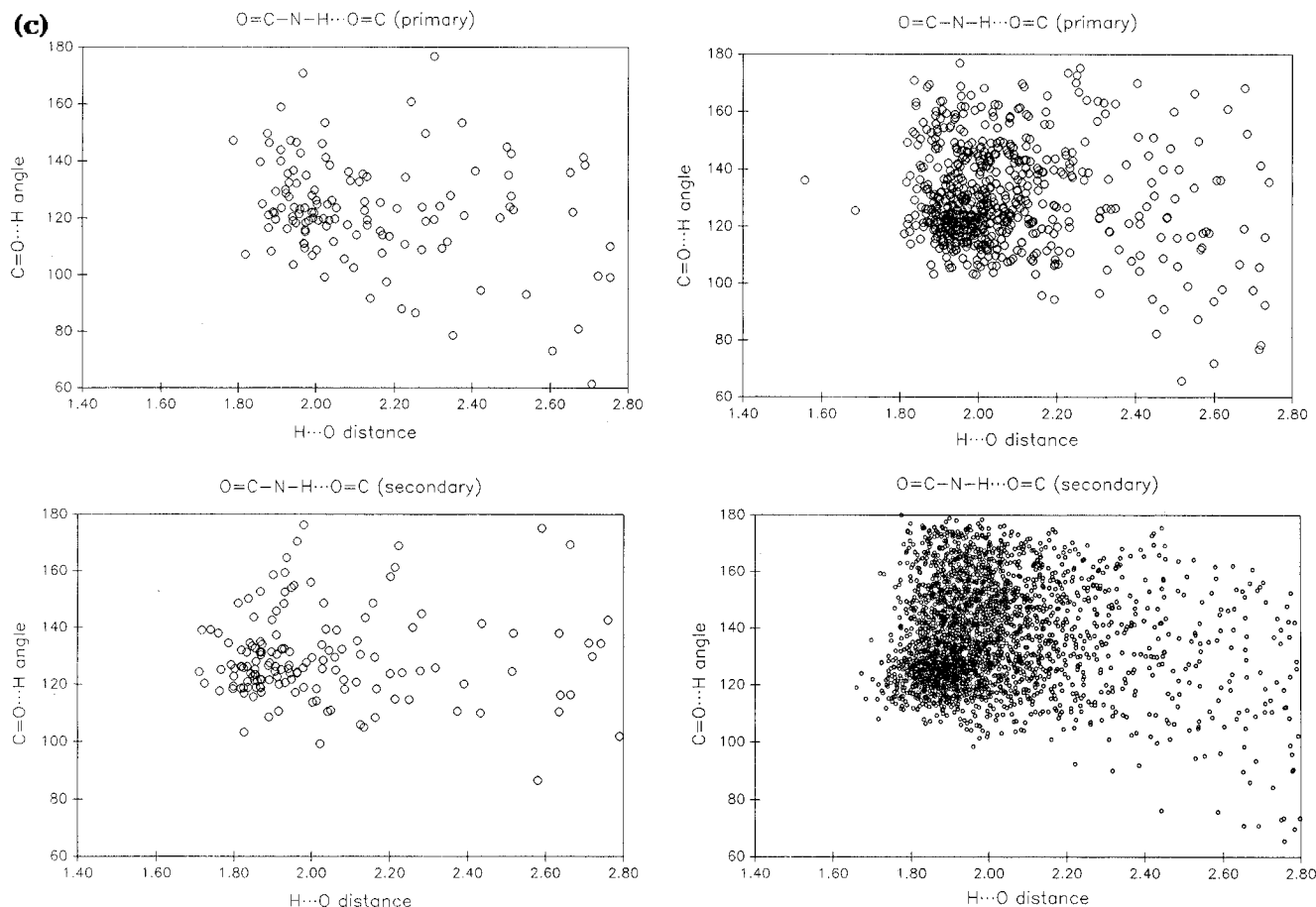


Figure 3. (a) Distribution of C=O...H angles in category B from primary and secondary OM (left-hand side) and organic amides (right-hand side). Note the distinct maxima at 130°. (b) The same distribution as in (a) after having applied the solid angle correction ($\sin \varphi$ factor). (c) C=O...H angle distributions versus NH...O distance range for primary and secondary OM (left-hand side) and organics (right-hand side). Note that a particular directionality is preferred for both short and long hydrogen bonds.

as the distance decreases. For NH...O distances shorter than 2.0 Å there are no ψ angles smaller than *ca.* 140°, and as the hydrogen-bonding interaction becomes shorter, the angles approach linearity. These parameters are well correlated, and shorter H...O distances are invariably associated with more linear hydrogen bond geometries. This feature, characteristic of strong hydrogen bonding, arises from mutual repulsion of the electronegative atoms N and O which constitute the hydrogen bond^{2f} and is observed for secondary OM amides as well. The distribution is the same as in organic crystals. For secondary amides (Figure 2c,d) the tendency to afford hydrogen bonds shorter than for primary amides can also be appreciated.

C=O...H Angles (φ) and Hydrogen Bond Directionality. The distribution of C=O...H angles [φ] in category B from primary and secondary OM and organic amides is shown in Figure 3a. Distinct maxima are observed at 130°. In order to take into account the solid angle correction,¹⁷ the distributions in Figure 3a were corrected by the $\sin \varphi$ factor to give the histograms in¹⁸ Figure 3b.

This procedure reveals interesting differences between OM and organic amides and between primary

and secondary amides. While the histograms for OM amides (both primary and secondary) clearly show double maxima at 130° (corresponding to a “ketonic” approach of the H-atom) and at 180° (corresponding to a linear approach), those for the pure organic primary amides retain only the single maximum at 130°. These effects are blurred for the organic secondary amides, where the distribution of φ values is almost uniform in the range 130–180°. These variations again hint that a steric factor is operating. It seems that the more highly hindered OM amides are unable to accommodate the (electronically favorable) “ketonic” approach and settle for the linear approach. Again, for the pure organics, secondary amides are by definition more sterically hindered than primary amides and therefore have a greater tendency to adopt the linear hydrogen bond geometry. For primary organic amides the presence of two amido hydrogens, coupled with the absence of steric hindrance in the amide region of the molecule, results in an optimization of a large number of hydrogen bonds with the ideal “ketonic” approach. Finally, it may also be noted that these φ angle distributions are insensitive to the H...O distance range; that is, a particular directionality is preferred for both short and long hydrogen bonds (Figure 3c). This kind of behavior is characteristic of strong OH...O and NH...O hydrogen bonds and is not observed for CH...O hydrogen bonds, for which bond directionality is distance dependent.¹

Tertiary Amides. Organometallic complexes containing tertiary amido groups are the most common (510

(17) Kroon, J.; Kanters, A. *J. Mol. Struct.* **1975**, *24*, 109.

(18) The solid angle correction takes into account the different probability of an angular distribution in order to upweigh the more linear contacts, which sweep a smaller solid angle. Obviously, this procedure is more important when a comparison between calculated and observed angular distributions is required.

(19) Acceptor bifurcation is likewise possible in donor-rich systems.¹

hits). Although, of course, there is no possibility for hydrogen-bonding donors, the groups still carry acceptor oxygen atoms. We have found that 28 REFCODES correspond to structures where the amide oxygens accept hydrogen bonds from OH groups (generally belonging to water molecules). These O---HO bonds are usually short (22 hits below 1.88 Å); the C=O---H angle is spread around 120° (at the amide oxygen), whereas the O(amide)---H---O angle tends to be more linear (above 150°). Of course, tertiary amides could be examined in other intermolecular patterns such as O(amide)---HC and O(amide)---HN; this will be the specific subject of a future study.

Hydrogen-Bonding Patterns in Selected Crystalline Amide Complexes. Selected examples will now be discussed. The aim of this section is to provide a direct perception of the geometric arrangements of organometallic amide complexes in crystals and of the patterns of hydrogen-bonding interactions by means of geometric analysis and graphical representation. Structural parameters for the hydrogen bonds are given as A---H---X, where A = donor, X = acceptor, distances in the sequence A---X, H---X (if the H atom position is available), and the angle A---H---X. Atomic labeling attributed by the CSD is maintained. The chemical and structural formulas, as well as the references to the original structural determinations, for all the species described in this section are provided as Supporting Information.

Primary Amides. The Mn complex (cyclopentadienyl)carbonylnitrosylcarbamoylmanganese (CPCNMN) is a representative example because it forms cyclic amide ring systems in its crystals. The metal carries one CO and one NO ligand, one η^5 -coordinated C₅H₅ (Cp) ligand, and one formamide moiety bound to the metal via a M---C σ -bond. One amide hydrogen (H(7)) establishes a cyclic dimer by interacting with the amide oxygen of a second molecule (N2---H7---O2 2.95, 1.93 Å, 176.5°), as shown in Figure 4a. It is interesting to observe that formamide²⁰ also forms cyclic dimers, as shown for comparison in Figure 4b, the N---O separation, however, being shorter in formamide (2.88 Å) than in the CPCNMN complex. Apart from this basic feature, which bridges organic and OM amides directly, there are interesting aspects which deserve attention. The second amide hydrogen does not participate in intermolecular interactions but points toward the N-atom of the NO group. The amide oxygen, in contrast, establishes an additional link (which probably takes the place of the second NH---O interaction commonly observed in primary amides) with an H-atom belonging to the Cp ligand (C3---H3---O2 3.33, 2.39 Å, 145.2°). A second CH---O noteworthy interaction has been found between a CO ligand and a Cp hydrogen (C4---H4---O1 3.33, 2.44 Å, 139.4°); this is not surprising, as Cp hydrogens have been found in our previous study to be particularly prone to forming intermolecular CH---O interactions with a CO ligand acceptor.¹

The flat Cu complex (bis(oxamido)trisulfane-*N,N,O,O*)-copper(II) (GEHRAM) crystallizes together with a dimethylformamide molecule. There are two primary amide groups, belonging to a large macrocycle, which interact directly with the metal atom *via* the two amido oxygens. These atoms participate in two different types of cyclic systems based on the interaction of each O-atom

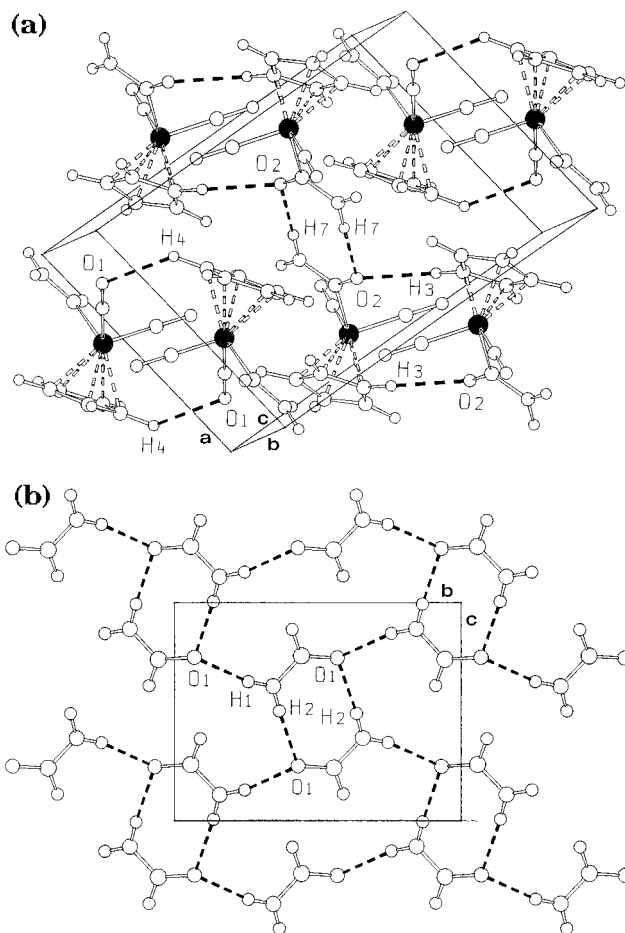


Figure 4. Cyclic amide ring in crystalline CPCNMN (a) and comparison with the cyclic dimers present in crystalline formamide (b). In (a) note also the NH---O(amide) and CH---O(carbonyl) interactions.

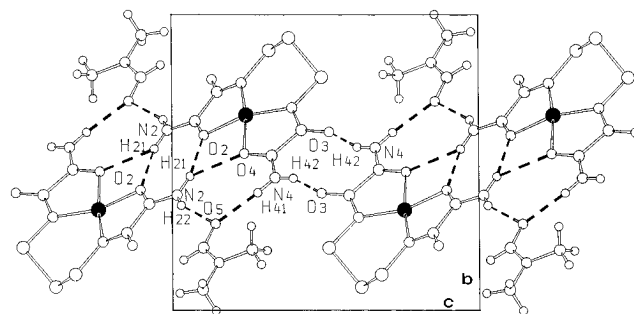


Figure 5. The two different types of cyclic systems present in crystalline GEHRAM: an 8-membered ring (N2---H21---O2) and a 10-membered ring, the latter using the ketonic oxygen O3 and the second amido group N4. Note how the dimethylformamide molecules interact with two molecules of the complex.

with its own amido group as shown in Figure 5. The first cyclic system is N2---H21---O2 (2.99, 2.08 Å, 159.4°), in which O2 is bound to the metal atom; the second ring is larger and utilizes the ketonic oxygen O3 and the second amido group nitrogen N4. In this 10-membered ring the N---O separation is shorter than that within the more conventional N2---H21---O2 six-membered ring (2.84 versus 2.99 Å). O1 participates only in intramolecular interactions (O1---N2 2.89 Å), whereas O4 forms a long bond with N2 via H2 (N2---O4 3.08 Å). The dimethylformamide molecule is found "bridging" two molecules of the complex in the crystal *via* NH---O-(formamide) interactions (N2---O5 2.89, N4---O5 2.91 Å).

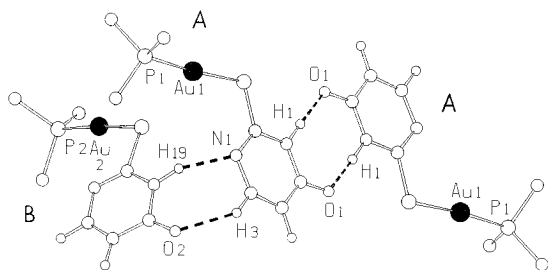


Figure 6. Hydrogen-bonding interactions in crystalline VAMGUL. The interaction A---A is based on an amide–amide ring; the interaction A---B is based on one NH---N bond and one >C=O---HC bond. For the sake of clarity, only the C-atom bound to phosphorus is shown for each phenyl ring of the PPh₃ ligands.

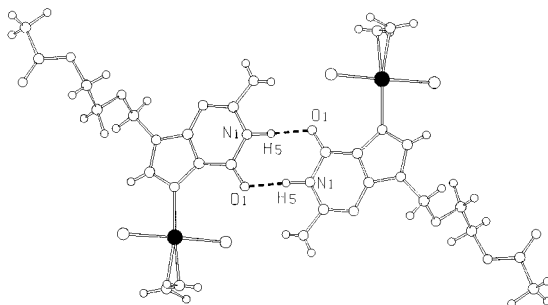


Figure 7. Eight-membered amide rings formed by the secondary amide moiety in crystalline SOFYOB.

Secondary Amides. The asymmetric unit of crystalline (2-thiouracilato-*S*)(triphenylphosphine)gold(I) (VAMGUL) contains two independent molecules (identified as molecules A and B for the sake of the present discussion). The Au complex carries a secondary amido group belonging to the diazo ketonic six-membered ring bound to the *S*-atom. The amido group of molecule A forms a cyclic dimer between two A-type molecules related by a center of inversion (N2–H1---O1 2.72, 1.64, 177.9°). The same moiety belonging to molecule B, however, does not form a similar cyclic system but clings to molecule A by donating the amido hydrogen to the “non-amidic” N-atom of the ring (N1). A seven-membered ring is formed *via* a second hydrogen bond between the amido O-atom and the H-atom bound to carbon. In other words, the interaction A---A is based on an amide–amide ring, while the interaction A---B is based on one N–H---N bond and one >C=O---H–C bond (see Figure 6). This second cyclic system, however, is not as tight as the amide ring (N4–H19---N1 2.96, 1.94 Å, 156.3°; C4–H3---O2 3.17, 2.27 Å, 139.4°). VAMGUL allows a sort of internal comparison between three types of hydrogen bonds involving the same system and allows us to rank these bonds in terms of metric parameters if not of energy: NH---O > NH---N > CH---O. This trend is expected, and there is no evidence in VAMGUL of any CH---N interaction below 2.8 Å.

The secondary amide moiety in crystalline *trans*-(acetylacetyl)chloro(ethylene)platinum(II) (SOFYOB) also forms amide rings, as shown in Figure 7. The metric parameters are strictly comparable to those in VAMGUL (N1–H5---O1 2.73 Å, 171°). A second aspect of interest is the participation of the Cl-atom coordinated to the Pt-atom in N–H---Cl bonds involving the NH₂ group protruding from the bicyclic system (H7---Cl2 2.60 Å, 164°). A number of intermolecular C–H---O links may also be detected.

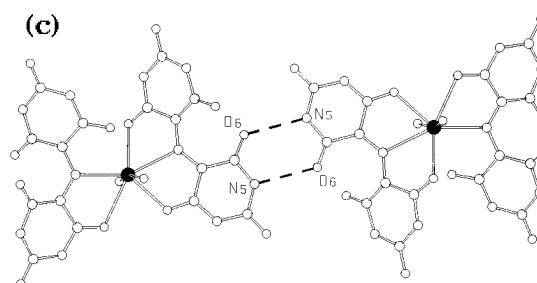
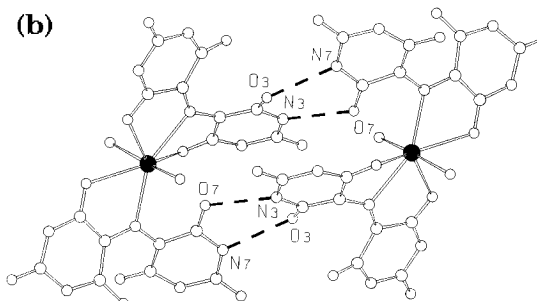
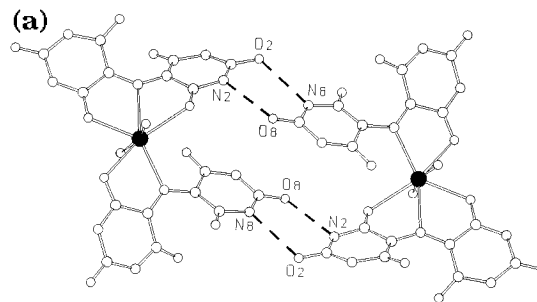


Figure 8. The five cyclic amide–amide systems in crystalline APURCD. Both rings 1 (a) and 2 (b) contribute twice to intermolecular interlocking because of the inversion center (N2---O8 2.82, N8---O2 2.96 Å). Cycle 3 (c) is located around another center of inversion (N5---O6 2.90 Å).

The Cd complex diaquabis(purpurato)cadmium dihydrate (APURCD) forms a remarkable hydrogen-bonding network in its crystal. Each molecule takes part in a grand total of five cyclic amide systems. Additional reinforcement is afforded by two other NH---O bonds (3.00 and 2.88 Å) and by four O–H---O bonds involving the two water molecules coordinated to the Cd metal (O13–H9---O15 2.74, O13–H10---O2 2.87, O14–H11---O11 2.80, O14–H12---O6 2.87 Å); the O-acceptors are on the same ligand. The five cyclic systems differ slightly in terms of their metric parameters: rings 1 and 2 (see Figure 8a,b) contribute twice because of the inversion center (N2---O8, 2.82, N8---O2 2.96 Å) linking two molecules, as shown in Figure 8b. Cycle 3 is located around another center of inversion (N5---O6 2.90 Å), as shown in Figure 8c. Atoms N9 and N10 also donate H atoms to neighboring molecules (N9---O5 3.00, N10---O13 2.88 Å). These bonds are between N–H and ketonic O-atoms as well as those forming the amide rings. It can be seen that donor–acceptor distances are comparable in all these systems.

Complexes Containing H₂O Molecules as Ligands. The complex diaquabis(formato)bis(nicotinamide)cadmium (AFNICD) forms ribbons of centrosymmetric cyclic dimers of type 4 as shown in Figure 9a (N2---O1 2.95 Å). Interribbon links are otherwise provided by the formate and water molecules, which also constitute large cyclic systems made up of 12 atoms (O10---O1 2.84 Å). Other links are provided by interac-

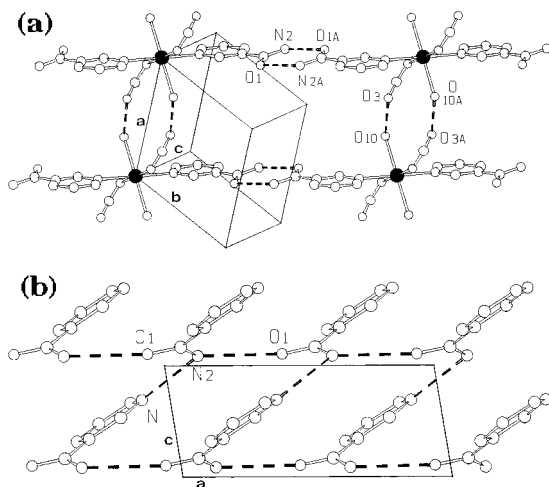


Figure 9. The ribbons of centrosymmetric cyclic dimers of category D present in crystalline AFNICD and the interribbon links between the formate and the metal-coordinated water molecules (a). Molecular layers above and below the plane of the drawing fill in the apparent voids in the network; H-atoms are omitted for clarity. In crystalline nicotinamide (NICOAM) there are no cyclic dimers but the NH_2 group participates in one $\text{N-H}\cdots\text{N}$ bond between the ring N-atom and the amido group and in one $\text{NH}\cdots\text{O}$ bond (b).

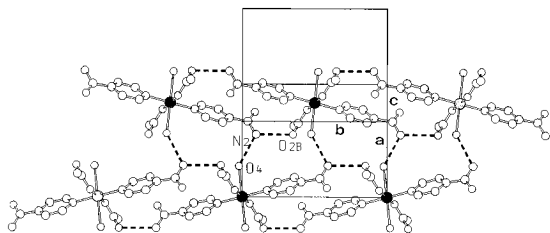


Figure 10. Packing motif in the crystalline complex BEXPV10. Note how the amide protons do not bind amido oxygen atoms; rather, two interactions are formed—one with a ligated water molecule and one with the ester oxygen.

tions between the water molecules and formate groups and the amido residues ($\text{O10}\cdots\text{O3}$ 2.76, $\text{N2}\cdots\text{O3}$ 2.98 Å, where O3 belongs to the formate group). Although these are the fundamental interactions in crystalline AFNICD, additional links are formed via the $\text{C-H}\cdots\text{O}$ interactions between the formate oxygen bound to the metal atom and the C-H groups of the nicotinamide rings. Thanks to these interactions, the molecular layers are also ligated, *viz.* the hydrogen bonding provides a truly three-dimensional network in the crystal. It is worth comparing this network with that present in crystalline nicotinamide (NICOAM), where no cyclic dimers are observed but the NH_2 group participates in one $\text{N-H}\cdots\text{N}$ bond between the ring N-atom and the amido group and in one $\text{NH}\cdots\text{O}$ bond, as shown in Figure 9b.

The packing motif in the complex bis(acetato)bis(amidoisonicotinato)diaquacopper(II) (BEXPV10), whose structure is related to that of AFNICD, is also based on a double interaction of the NH_2 groups and not on dimers (see Figure 10). In this case, however, it can be noted that the packing diagram achieves the optimization of all interactions with the participation of all the donor and acceptor groups available in the structure ($\text{NH}\cdots\text{O}$, $\text{OH}\cdots\text{O}$, $\text{CH}\cdots\text{O}$, etc.). In fact, the amide protons do not bind amido oxygen atoms; rather, two

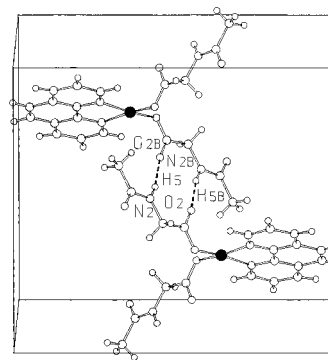


Figure 11. For crystalline ACGLCU, amido oxygen atom participation in an interaction with the keto group of the ester which is in a position β to the amide N-H , thus forming a cyclic dimer which involves 10 atoms. The amide oxygen atom is involved in $\text{CH}\cdots\text{O}$ hydrogen bonding.

interactions are formed—one with the oxygen of a ligated water molecule ($\text{N2}\cdots\text{O4}$ 2.92 Å) and one with the ester oxygen ($\text{N2}\cdots\text{O2B}$ 2.89 Å).

In crystalline bis(acetato)bis(amidoisonicotinato)diaquacopper(II) (FUWGIN) the packing arrangement is the same as in BEXPV10, with the far from trivial difference that the amide proton is also bound to the amide oxygen ($\text{H2}\cdots\text{O1}$ 2.24 Å). This indicates that, in terms of energy and crystal cohesion, there is ample structural variability when the choice is between amide–amide interactions and amide–water interactions.

Finally, the packing motif in crystalline bis(*N*-acetylglucinato)(1,10-phenanthroline)copper(II) (ACGLCU) can be discussed. In this complex the amide hydrogen participates in an interaction with the ester C=O which is in a position β to the amide N-H , this resulting in a cyclic dimer which involves 10 atoms, as shown in Figure 11. The amide oxygen atom is involved in $\text{CH}\cdots\text{O}$ hydrogen bonding.

Conclusions

Organometallic systems combine the intra- and intermolecular bonding features of organic fragments (the ligands) with the rich coordination chemistry of transition-metal atoms. The resulting structural and chemical variability is enormous, and there is an increasing awareness that this structural variability can be advantageous in the construction of solids with predefined structural arrangements. It has been widely demonstrated on organic systems that this goal can be achieved by choosing appropriate patterns of intermolecular interactions such as those established by hydrogen bond donor and acceptor groups. Preliminary results in the construction of organic–organometallic solids are encouraging.²¹ We have been able to demonstrate that much of the knowledge on the intermolecular interactions in organic systems can be transferred to the engineering or organometallic solids with some, far from trivial, differences arising essentially from the presence of acceptor and donor groups typical of organometallic systems (such as CO, NO, CN, and the π -bond unsaturated cyclic ligands) as well as from the rather common occurrence of charged species.²² Our

(21) (a) Braga, D.; Grepioni, F.; Byrne, J. J.; Wolf, A. *J. Chem. Soc., Chem. Commun.* **1995**, 1023. (b) Braga, D.; Costa, A. L.; Grepioni, F.; Scaccianoce, L.; Tagliavini, E. *Organometallics*, in press.

efforts are, at the moment, chiefly concentrated on the appreciation of these similarities and differences.

In this paper we have explored the NH...O intermolecular hydrogen bonds established by primary and secondary amido groups constituting (or belonging to) ligands coordinated to transition-metal atoms. The results of our survey can be summarized as follows:

(i) The hydrogen bond patterns formed by OM complexes containing amido groups are of a wider variety than that found in pure organic amides. The principal hydrogen bond patterns found in the organics are all observed for the organometallics, but the presence of water, counterions, and more bulky molecular skeletons leads to a greater variability of interactions.

(ii) The database studies show that the "average" hydrogen bond in OM amido complexes is longer than in pure organic species, although, to compensate, there

(22) (a) Braga, D.; Calhorda, M. J.; Dyson, P.; Grepioni, F.; Johnson, B. F. G.; Sanderson, F. M.; Veiros, L. *Organometallics* **1995**, *14*, 121. (b) Braga, D.; Grepioni, F.; Byrne, J. J.; Calhorda, M. J. *J. Chem. Soc., Dalton Trans.* **1995**, 3287.

is a greater number of hydrogen bonds *per* molecule because of the more frequent occurrence of bifurcation.

(iii) In the OM amido complexes a greater proportion of hydrogen bonds tend to linearity, perhaps because of steric factors.

(iv) Examination of individual crystal structures shows that, in addition to NH...O hydrogen bonding, CH...O interactions confer additional stabilization and confirm the tendency to link together hard with hard (the amido groups) and soft with soft (CH groups and CO ligands) donors and acceptors.

Acknowledgment. Financial support from the MURST (D.B., F.G.), DST (G.R.D.), and UGC (K.B.) is acknowledged.

Supporting Information Available: Structural and chemical formulas, bibliographic references for the selected compounds discussed in this study, and comparative histograms for charged and neutral OM compounds containing primary and secondary amido groups (5 pages). Ordering information is given on any current masthead page.

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