The crystal packing of bis(2,2′-dipyridylamido)cobalt(II), Co(dpa)$_2$, is stabilized by C–H···N bonds: are there any real precedents?

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A crystallographic study of Co(dpa)$_2$ reveals that the pseudo-tetrahedral molecules stack together to form a one-dimensional ribbon with the molecules linked together through significant C–H···N interactions; the C···N separation is 3.41(3) Å and the angle at the hydrogen atom is 177(2)°.

While studying the varied behavior of 2,2′-dipyridylamine, Hdpa, and its anion dpa$^-$, in cobalt complexes[1] we prepared† and structurally characterized‡ the pseudo-tetrahedral complex Co(dpa)$_2$, shown in Fig. 1. The two dpa anions are related by a crystallographic twofold axis and each is nearly planar; the dihedral angle between the two pyridyl rings within the ligand is only 3.6°. This feature is similar to that found for the copper analog.[2]

An analysis of the packing of the molecules in the crystal (Fig. 2) shows a prominent characteristic: the molecules stack in a way that gives an extended array with relatively short C(6)–H(6)···N(2B) contacts. The distances obtained from the X-ray diffraction studies are C(6)–H(6) 0.97(3) Å, H(6)···N(2B) 2.44(3) Å and C(6)···N(2B) 3.41(3) Å; the angle at the hydrogen atom is 177(2)°.

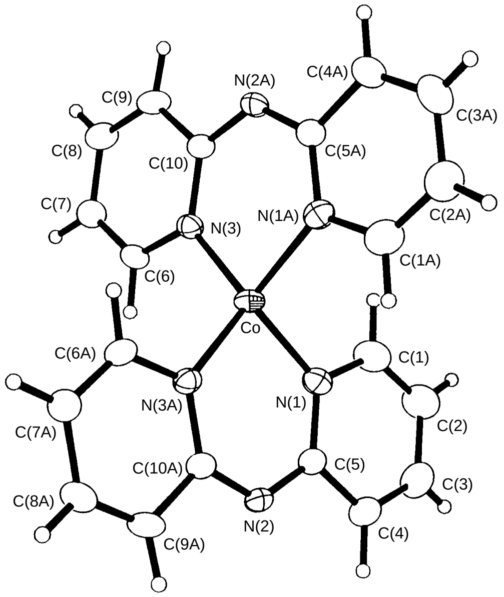


Fig. 1 Molecular structure of Co(dpa)$_2$. Selected bond lengths (Å) and angles (°): Co–N(1) 1.972(2), Co–N(3) 1.963(2), N(1)–C(1) 1.364(4), N(1)–C(5) 1.367(4), N(2)–C(5) 1.346(4), N(2)–C(10A) 1.344(4), N(3)–C(6) 1.378(4), N(3)–C(10) 1.371(4); N(3)–Co–N(1) 120.66(9), N(3A)–Co–N(1) 94.5(1), C(10A)–N(2)–C(5) 128.2(2).

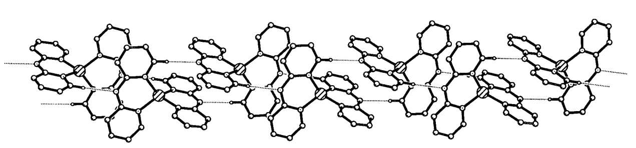


Fig. 2 Packing diagram of Co(dpa)$_2$ viewed along the *a* axis showing the C–H···N bonds; C···N 3.41(3) Å, C–H 0.97(3) Å, N···H 2.44(3) Å, C–H···N 177(2)°

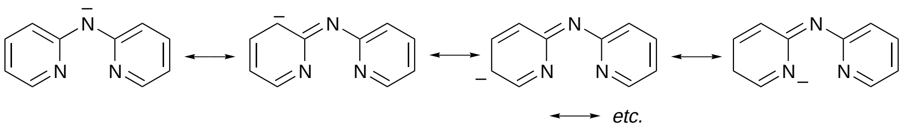
The questions that immediately arise are: how do these distances compare to those in other compounds with C–H···N interactions, and is it 'truly' a hydrogen bond? A superficial check of the literature quickly gives several references to 'C–H···N hydrogen bonds'.[3] However, as one starts to dig into the references to find the 'real examples' they are not easily found. Taylor and Kennard[4] give a few references to such bonds based on neutron diffraction studies. They assumed that C–H···N distances between 2.522 and 2.721 Å were indicative of hydrogen bonding. In their data, C–H···N angles varied from 157.3° to as low as 124.6°. Another system, which contains 1,3,5,7-tetrabromoadamantane, hexamethylenetetramine and CBr$_4$[5] is said to have a C–H···N bond when the C···N distance is 3.77 Å and the angle at the H atom is 151°.

Of course, the importance of hydrogen bonding is unquestionable in many aspects of chemistry,[6] particularly for so-called crystal engineering. As a result of the excitement in this field, the distinction between a simple classical van der Waals interaction and a hydrogen bond is being continuously blurred. A 'hydrogen bond' is regarded as 'any cohesive interaction X–H···Y, where H carries a positive and Y a negative (partial or full) charge',[7] where the angle at H can be anything > 90°, and consequently a 'very distorted geometry cannot be regarded as anomalous'.[8]

This type of very loose working definition has led to the proliferation of very questionable claims of 'hydrogen bonds' such as C–H···O in compounds where the C···O distance is 3.60 Å and the angle at H is 136°[9] or C···O of 3.82 Å and an angle of 154°.[10] Another recent example is the suggestion of 'intermolecular C–H···C interactions' in a complex which has a C···C distance of 3.83 Å and an angle at the H atom of 159°.[11]

It is clear that the field is getting muddier and muddier as the definition of a hydrogen bond is relaxed. What is not clear is why it is justified to continue to publish communications regarding this topic. We strongly disagree with the newer and more relaxed definitions that do not distinguish between a 'hydrogen bond' and what is nothing more than a classical van der Waals interaction.

In Co(dpa)$_2$, the linearity of the C–H···N moiety and the short N···H distance of 2.44 Å are possibly an indication of a relatively important hydrogen bonding interaction, especially when one takes into account that the C–H distance, as determined by X-ray crystallography, is roughly 0.10 Å shorter than the actual distance to the proton that would be determined by neutron diffraction.[12] Consequently, the probable N···H distance is about 2.33 Å. This value is among the shortest of the C–H···Y, Y = N or O distances.[13] A similar N···H interaction is also present in Cu(dpa)$_2$; the distance obtained from an X-ray crystallographic study is 2.52 Å. The reason why a short and possibly real C–H···N hydrogen occurs in Co(dpa)$_2$ is that the N atom doubtless bears a considerable amount of negative charge.



Scheme 1

From a valence bond resonance point of view, it appears that distribution of the negative charge on the dpa$^-$ ion away from the N atom from which the proton has been removed is not likely to be very complete, as shown in Scheme 1.

In the case of Co(dpa)$_2$ we believe that it is justified to invoke the existence of a C–H···N hydrogen bond. The sum of the van der Waals radii of H and N (1.2 + 1.5 = 2.7 Å) is significantly longer than the distance found (2.41 Å). Moreover, the C–H···N unit is very nearly linear. In most, if not all, of the previously claimed examples of C–H···N 'hydrogen bonds' the contact is little (or no) different from that expected for an ordinary, classical van der Waals contact and the angles at the H atom are well below (often far below) 180°. While the literature contains numerous allusions to C–H···N 'hydrogen bonds' there seems little if any reason to accept this description. Or, to invoke the parable of the emperor's new clothes, the question of why many people seem to find the emperor well dressed despite any persuasive evidence that he isn't naked, arises. In the packing of molecules containing both C–H bonds and N atoms, there seems to us to be no reason whatever to refer to perfectly normal van der Waals contacts between the two as 'hydrogen bonds'.

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Footnotes and References

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† In a 100 ml round-bottom flask, 0.963 g (5.62 mmol) of Hdpa was dissolved in 30 ml of toluene. The solution was cooled to −78 °C and 4.1 ml of 1.4 M MeLi was added. The solution immediately turned milky white. The reaction mixture was warmed to near room temp. upon which 0.344 g (2.64 mmol) of anhydrous CoCl$_2$ was added from a solid addition tube. After several min of stirring, 20 ml of thf was added forming a dark red–brown solution. The reaction was stirred overnight at room temp. The majority of the product precipitates from solution as an orange powder. It was collected by filtration, washed twice with small amounts of thf, and dried under vacuum to yield 0.700 g (66.4%) of Co(dpa)$_2$. Crystals were obtained from work-up of the filtrate. The filtrate was evaporated to dryness and then dissolved in 25 ml of toluene to give a deep red-wine solution. This solution was filtered through Celite and layered with 40 ml of hexanes. Red crystals (0.0395 g, 3.75%) grew after two weeks of diffusion. IR (KBr, cm^{-1}): 3051w, 1609s, 1533s, 1440vs, 1250m, 1241m, 1146s, 1111w, 1095w, 1045w, 1006s, 894m, 849m, 786m, 767s, 733m, 726m, 656w, 553w. UV–VIS (CH$_2$Cl$_2$): λ = 390, 355, 342 nm.

‡ *Crystal data* for Co(dpa)$_2$: crystal dimensions 0.18 × 0.15 × 0.13 mm, $C_{20}H_{16}CoN_6$, M = 399.32, monoclinic, space group $I2/a$, a = 12.325(1), b = 10.689(5), c = 14.229(1) Å, β = 107.94(1)°, U = 1783.4(9) Å^3, Z = 4, D_c = 1.487 g cm^{-3}, μ(Mo-Kα) = 0.980 mm^{-1}. Data were obtained at 213(2) K on a Nonius FAST diffractometer. A total of 1164 unique reflections were collected using ellipsoid-mask fitting within a 2θ range of 45.06°. The structure was solved by the Patterson method and refined by full-matrix least squares on F^2. All hydrogens were located from Fourier difference maps and their positional and thermal parameters were refined. The final refinement converged to R_1 = 0.038 and wR_2 = 0.079 (for 1164 data and 155 parameters). CCDC 182/500.

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