Chemical Bonding

DOI: 10.1002/anie.201403078

Dative or Not Dative?

Daniel Himmel, Ingo Krossing, and Andreas Schnepf*

bond theory · dative bonds ·
p-block coordination compounds

The critique on our Essay *Dative Bonds in Main-Group Compounds: A Case for Fewer Arrows!*[1] by Prof. Gernot Frenking (GF) (*Dative Bonds in Main Group Compounds: A Case for More Arrows*)[2] gives us the opportunity to clarify some points. First of all, we refuse a single-sided notation on principle when a balanced view from different sides is necessary for complete understanding. This was the central issue behind our Essay.[1]

Formal versus partial charges: The fact that, as mentioned by GF, Lewis structures and their formal charges ”do not provide direct information about the actual charge distribution in a molecule” is taught to “every student in a freshman chemistry course” in Tübingen and Freiburg as well as in Marburg and supposedly everywhere. However, Lewis formulae with formal charges can point to a polarization component, which amends the charge distribution expected based on electronegativities. A textbook example is the molecule $\mathrm{:C{\equiv}O:}$, in which the negative formal charge at C hints to a carbon atom that—in contrast to the carbon atom in acetone or CO_2—is not positively polarized. For bonds with a more ionic character, one may also consider resonance structures in which some of the atoms are not covalently bonded, for example, in $[BF_4]^-$ (Figure 1).

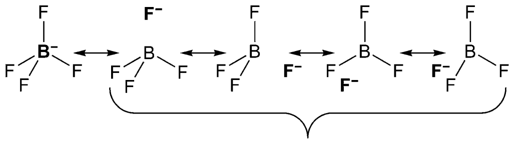
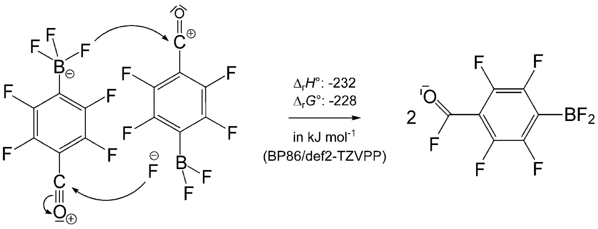


Figure 1. Resonance structures for $[BF_4]^-$. In each of the resonance structures grouped in brackets one atom is not covalently bonded.

In organic chemistry, resonance structures with formal charges are frequently used as a tool, for example, to illustrate directing effects in aromatic substitution reactions. However, as in the case for $[N(PPh_3)_2]^+$ when electronegativities and the negative formal charge on the N atom in the most important conventional resonance structure both agree with the calculated charge distribution, it appears grotesque to speak of “N^+”.

Misled by dative notation? In a paper that appeared in 2012[3] the structures and properties of compounds that are zwitterionic in conventional formulation were calculated and interpreted as doubly dative bound donor–acceptor complexes “$L{\rightarrow}C_6F_4{\rightarrow}BF_3$”. The abstract explicitly states: “The complexes $[OC{\rightarrow}C_6F_4{\rightarrow}BF_3]$ and $[N_2{\rightarrow}C_6F_4{\rightarrow}BF_3]$ are predicted to be thermodynamically stable.” In support, the decomposition reactions to monomeric (!), gaseous singlet C_6F_4 were calculated. The established zwitterionic notation reveals the possibility for the exothermic and exergonic abstraction of fluoride through the Lewis acidic carbon atom [Eq. (1)]. For space reasons, in Equation (1) only two of the many possible resonance structures of $OC\text{-}C_6F_4\text{-}BF_3$ are used. The use of well-balanced Lewis structures directly points to this reaction, which was completely neglected in the Ref. [2]. Analogously, the classical notation readily suggests the strongly exothermic/exergonic (−187/−228 kJ mol^{-1}; BP86/def2-TZVPP) decomposition of the diazonium trifluoroborate zwitterion $NN^+{-}C_6F_4{-}BF_3^-$ into the expected products $C_6F_5{-}BF_2$ and N_2. Thus, the exclusive use of the dative notation disguises the chemical reactivity and masks naturally expected subsequent reactions, which might easily have been deduced a priori from the above Lewis structures (more examples are given in Ref. [1]).



(1)

Put calculations and analyses aside! Is it really necessary to turn on a computer and do a quantum chemical calculation in order to describe the bonding in a molecule? Bonding concepts should be understandable on their own and even be useful in a high school chemistry class. Thus, a concept should be insightful even with quick notation on a napkin.

Well, what is a dative bond? GF states: “Dative bonds can be very strong and short and they may be associated with a significant charge transfer”. He sees recent work not as a disagreement with, but as “an extension of the knowledge

---

[*] Dr. D. Himmel, Prof. Dr. I. Krossing
Institut für Anorganische und Analytische Chemie
und Freiburger Materialforschungszentrum (FMF)
Universität Freiburg
Albertstrasse 19, 79104 Freiburg (Germany)
Prof. Dr. A. Schnepf
Universität Tübingen (Germany)

about dative bonds". From our point of view, the strong dative bond evoked by GF is simply a synonym for a normal bond which, if necessary, requires ionic mesomeric structures for its complete description.

We stick to Haaland's[4] notion: The basic characteristics of a dative bond, depicted with an arrow "→", are its weakness, the substantially longer bond length compared to typical single bonds, and a rather small charge transfer. Consequently, GF's "extension of the knowledge" appears to us not only as a contradiction, but effectively as a circular argument. We do not condemn the use of dative notation and consider it to be very useful and valuable in many cases. However, it should be put into context so that the benefits for the bond description are apparent. If one wants to highlight a particular aspect of a compound—also as a thought experiment like that developed by GF—one can do this. However, the compound should not be marketed under this aspect, as Figure 2 illustrates tongue in cheek…

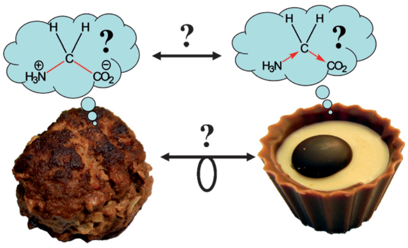


Figure 2. An analogy of semantics. One can designate a meatball as an animal praline, but you wouldn't expect to find it next to the chocolates in the supermarket.

In this response we also take the opportunity to correct one point in our original Essay: Professor Thiel from the Max-Planck-Institut für Kohlenforschung in Mülheim noted that we misquoted the title of the publication *Synthesis and Structure of Carbene-stabilized N-centered Cations $[L_2N]^+$, $[L_2NR]^{2+}$, $[LNR_3]^{2+}$, and $[L_3N]^{3+}$"* (*Chem. Eur. J.* **2013**, *19*, 3542–3546). Indeed, we interpreted the title, enforced by the notation in Scheme 1 in this publication, as a paraphrased ligand-stabilized N^{3+} and shortened the title of the publication incorrectly to this term. We apologize to the readers and especially to the authors of this paper for our inaccurate citation of the title.

Received: March 7, 2014

---

[1] D. Himmel, A. Schnepf, I. Krossing, *Angew. Chem.* **2014**, *126*, 378 – 382; *Angew. Chem. Int. Ed.* **2014**, *53*, 370 – 374.
[2] G. Frenking, *Angew. Chem.* **2014**, *126*, 6152 – 6158; *Angew. Chem. Int. Ed.* **2014**, *53*, 6040 – 6046.
[3] C. Goedecke, R. Sitt, G. Frenking, *Inorg. Chem.* **2012**, *51*, 11259 – 11265.
[4] Haaland, *Angew. Chem.* **1989**, *101*, 1017 – 1032; *Angew. Chem. Int. Ed.* **1989**, *28*, 992 – 1007.