

## Poster Presentation

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### *Identifying the correct d-block element with aspherical scattering factors*

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Element assignment in single-crystal X-ray diffraction (XRD) is based on the number of electrons of a particular atom, so that neighboring elements in the periodic table are often hard to distinguish. 3d-block carbene complexes, e.g. [1], provide examples where the situation is even worse: use of the independent-atom model (IAM) leads to significantly better figures of merit for the element left to the correct one in the periodic table, and the element can hence not be identified by XRD using the IAM without prior chemical knowledge. This is readily explained by the characteristics of the ligand, which can cause electron-deficiency at the metal center. Hence Cu instead of Zn gives a significantly better fit to the diffraction data in the IAM in our example, although the heavier element is unambiguously present. Rearrangements in the aspherical valence electron-density distribution (EDD) hence forbid to reliably distinguish and to correctly identify the metal atom in such coordination compounds with conventional methodology, whereas aspherical scattering factors allow a correct assignment. These findings clearly illustrate the need to sometimes go beyond "spherical-atoms". We show how "whole molecule" aspherical scattering factors derived from theoretical computations within the Hansen/Coppens multipole model EDD description [2a] can be successfully used in least-squares refinement. A related approach is Hirshfeld-atom refinement [2b], but for network structures, disordered molecules and those with atoms on special positions this approach is not always technically feasible. The suggested modeling procedure is based on the invariom database [3] and its capability to predict quantum chemical X-H bond distances involving hydrogen, and is amenable to d-block compounds where all-electron calculations are possible. Due to the important role of aspherical EDD in the vicinity of the central atom we expect that similar behavior will occur in linear and square-planar, but not in tetrahedral and octahedral coordination.

[1] A. P. Singh, P. P. Samuel, H. W. Roesky, M. C. Schwarzer, G. Frenking, N. S. Sidhu, B. Dittrich, *J. Am. Chem. Soc.* (2013), 135, 7324-7329., [2] (a) N. Hansen, P. Coppens, *Acta Cryst.* (1978), A34, 901 (b) D. Jayatilaka, B. Dittrich, *Acta Cryst.* (2008), A64, 383-393., [3] B. Dittrich, C. B. Hübschle, K. Pröpper, F. Dietrich, T. Stolper, J. J. Holstein, *Acta Cryst.* (2013), B69, 91-104.

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