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A brief history of scorpionates

When I was mulling on potential themes for a special issue, I wanted to feature a chemically important compound family wherein the structure has a palpable effect on reactivity. Perhaps pandering to my own personal experience, I decided scorpionates would be an ideal topic.

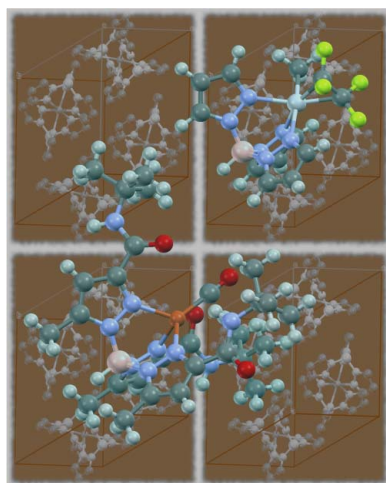
Before 1966 there were only a few examples of polysubstituted boron compounds with B–N bonds, with all of them behaving as noncoordinated spectator anions (Krause & Hawes, 1933; Smith & Kraus, 1951). In the seminal report by Trofimenko, a new class of chelating polypyrazolylborate ligands, specifically trispyrazolylborates (Tp), was created by reaction of potassium borohydride with three equivalents of pyrazole. The resulting anion was then observed to coordinate to a large range of divalent metal ions (Trofimenko, 1966).

The first crystal structure incorporating a Tp ligand was reported in 1970, namely bis[hydrotris(pyrazol-1-yl)borato]cobalt(II), which confirmed the *D*3*d* symmetric structure for bis-Tp complexes (Churchill *et al.*, 1970) previously theorized based on comparative transition metal complex series colors and molecular modeling (Trofimenko, 1967). In 1978, the first Tp structure to appear in an *Acta Crystallographica* journal, methyl[hydrotris(pyrazol-1-yl)borato]tetrafluoroethyleneplatinum, afforded an accurate stereochemical description to elucidate previously observed anomalous couplings in the NMR spectra (Rice & Oliver, 1978). The perfluoroalkyne analogue had been reported four years previously (Davies & Payne, 1974). Both of these platinum structures featured monoligand coordination similar to only a handful of first-generation Tp compounds (Thompson *et al.*, 1979; Roundhill *et al.*, 1979).

To combat the formation of bis-ligand complexes, a second generation of Tp ligands was introduced in 1986 wherein the 3-position of the pyrazole has a bulky alkyl or aryl substituent such as *tert*-butyl or phenyl. This modification prevented the interdigitation observed in bis-Tp complexes and allowed new tetrahedral complexes to be synthesized (Calabrese *et al.*, 1986).

In a 1993 review, Trofimenko notes the multidentate features of Tp and states, “Nature provides the closest analogy to these features in the scorpion. This creature grabs its prey with two identical claws and then may proceed to sting it with the sharp point of the curving tail. Therefore, I found it appropriate to coin the term ‘scorpionate ligands’...” (Trofimenko, 1993). While first- and second-generation scorpionates are still providing bountiful chemistry arising from facile tuning of electronics and sterics, Reger introduced yet another option, *viz.* third-generation scorpionates that are functionalized in the fourth, noncoordinating, back position on the B atom allowing, for instance, magnetic behavior modification of iron scorpionate complexes (Reger, 2005).

The first book on scorpionates, ‘*Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*’, intended to provide a 32-year comprehensive coverage of Tp chemistry up to 1998 (including some 1999 papers), was published in 1999 (reprinted in 2005) with 1568 references cited (Trofimenko, 1999). The second book, ‘*Scorpionates II: Chelating Borate Ligands*’ was published in 2008 to cover research from 1999 to 2008, a much shorter nine-year period, with 1710 references cited (Pettinari, 2008). A study of common ligand metrics showed that Tp ligands had the largest population, at the time the study was conducted, for *fac*-coordinating triskelion (*i.e.* tripodal) ligands and were second largest only to cyclopentadienide ligands for all tridentate ligands (Aguila, 2009). While much of Tp research, as is to be expected, is within the realm of classical chemistry, scorpionates could even be found in more general scientific endeavors. A recent paper shows a palladium scorpionate used in positron emission tomography (Lee *et al.*, 2011). A search on scorpionate structures in the Cambridge Structural Database (Version 5.34 of



May 2013; Allen, 2002) yields 3480 hits, of which 59 appear in *Acta Crystallographica* journals. I can confidently say that scorpionates are clearly valuable, prolific, ‘work-horse’ ligands. In his final remarks in the first scorpionate book, Trofimenko concludes with a sentiment which rings true even today, ‘In the final analysis, the scorpionate field is wide open, and can be extended in almost any direction, being restricted only by the creativity of the scientist.’ (Trofimenko, 1999).

Allow me to comment on the cover art at this point. The composite sepia background is from the packing diagram of a representative bis-Tp complex (Nakata *et al.*, 1995). The top molecule was generated from atomic coordinates from the first scorpionate to appear in an *Acta Crystallographica* journal (Rice & Oliver, 1978). The lower molecule is one of the most recent scorpionates, that is to say, a molecule from this issue!

Tony Linden, Section Editor of *Acta Crystallographica Section C*, asked me to scour the scientific community to look for ‘contributions that have something special to say.’ I believe I have persuaded some of the best authors in the field of Tp chemistry – or chemistry, in general, for that matter – many of whom have not submitted to an *Acta Crystallographica* journal previously. Together with our expert authors, I am pleased and honored to feature the chemistry of scorpionates and their kin in the first special issue of *Acta Crystallographica Section C*.

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