

Elaborating the Vocabulary of Coordination Chemistry

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1. Introduction

Having read the report by Daly *et al* in the April 2010 issue of *Angewandte Chemie* (1) concerning their recent synthesis of a new fifteen-coordinate complex of thorium with the tetradentate aminodiboranate anion (see figure) and their accompanying discussion of coordination number limits in other reported complexes, I was struck by the thought that their discussion, though highly competent and to the point, might be considerably enhanced through an elaboration of some of the traditional vocabulary used by coordination chemists. The purpose of this brief essay is to bring some of these suggested elaborations to the attention of the chemical community as a whole in order to stimulate a broader discussion of the accompanying issues.

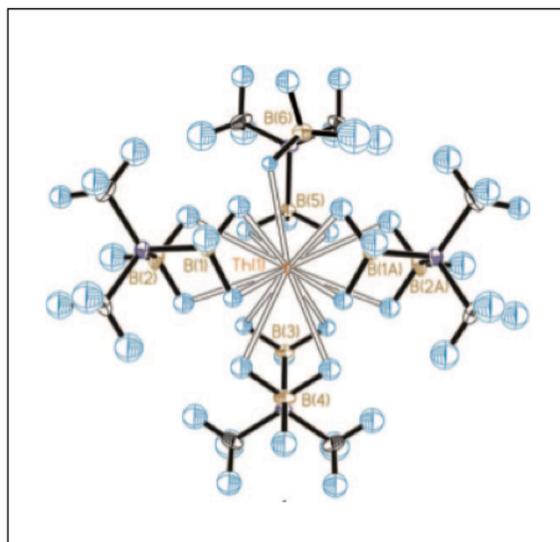
2. Which Kind of Coordination Number?

The specific point in the report by Daly *et al* which prompted these thoughts on the vocabulary of coordination chemistry involves the authors' mention of the compounds UCp_4 and $ThCp_4$ (1):

The compounds tetrakis(cyclopentadienyl)uranium [UCp_4] and its thorium analog [$ThCp_4$] are each connected to 20 atoms but the Werner complex number of 12 (counting π bonds as occupying one site) is widely acknowledged to be more appropriate to describe the metal-ligand bonding in these compounds.

It is apparent that, in this sentence, the authors are making a transition between two alternative definitions of the term "coordination number" – one involving the number of bonded ligand atoms and the other involving the number of ligand-metal bonding electron pairs.

However, I would go even further than this and argue that there are in fact, not just two, but rather three possible alternative definitions of coordination number, and that in discussions of this topic these three alternatives should always be carefully distinguished from one another through the use of an appropriate descriptive adjective. Indeed, I have been making such a distinction for many years in my own teaching, where I employ the



Tetrakis(aminodiboranato)thorium(IV) or $[Th(H_3BNMe_2BH_3)_4]$. Because of symmetry, only two of the three H atoms on each $-BH_3$ group are able to simultaneously act as EPDs relative to the Th center, thus making each aminodiboranate ligand tetradentate.

the self-evident terms: ligand coordination number (LCN), atom coordination number (ACN), and electron-pair coordination number (EPCN), depending on which aspect of the bonding and structure of a particular complex is under discussion (2).

In a traditional Werner complex, such as $Co(NH_3)_6^{3+}$, containing only simple monodentate ligands, all three of these coordination numbers are identical (3, 4). As first interpreted electronically by Sidgwick in the 1920s, the central Co^{3+} ion is surrounded by six bonding electron-pairs, and is, in turn, bonded to six nitrogen atoms and thus to six neutral NH_3 ligands (5). As a consequence, $LCN = ACN = EPCN = 6$ and there was little need at the time to distinguish between these three usages.

However, once one introduces the use of multidentate ligands, it is no longer true that the LCN is identical to the ACN and EPCN. Classic examples include the bidentate ethylenediamine complexes, $Co(en)_3^{3+}$, originally studied by Werner, for which LCN

= 3, but ACN = EPCN = 6, and the hexadentate ethylenediaminetetraacetate complexes, such as $\text{Ca}(\text{EDTA})^{2-}$, for which LCN = 1, but ACN = EPCN = 6, as well as the many other chelated systems originally studied by such pioneers as Gilbert Morgan and Gerold Schwarzenbach (6, 7).

And, finally, with the rise of organometallic chemistry in the 1940s and 1950s, the last of these three identities – that between the ACN and the EPCN – also broke down. Thus in the classic bis(cyclopentadienyl) iron(II) complex, $[\text{FeCp}_2]$, or ferrocene, all three coordination numbers are different: LCN = 2, ACN = 10, EPCN = 6 (8).

Applying these distinctions to the comparison of Daly *et al* between their newly synthesized $\text{Th}(\text{H}_3\text{BNMe}_2\text{BH}_3)_4$ complex and the compounds UCp_4 and ThCp_4 , we find that for the former LCN = 4, ACN = 15, EPCN = 15, and that for the latter LCN = 4, ACN = 20, EPCN = 12. Thus we see that the newly reported complex has a lower ACN than the previously reported pentadienyl complexes of uranium and thorium, but a greater apparent EPCN.

3. Which Kind of Ligand?

Our use of the qualifying term “apparent” in the previous sentence brings us to our second point, which deals with the nature of the ligands involved in these various complexes. As first pointed out by Sidgwick in the 1920s, the ligands in classical complexes, whether monodentate or multidentate, all act as electron-pair donors when bonding to the central ion of the complex and this electron-pair always corresponds to a lone or nonbonding pair on the isolated ligand (5). In other words, to use an overlooked suggestion by Gutmann, these ligands function as electron-pair donors or EPD agents (9). This observation was actually anticipated by G. N. Lewis, who used it as the basis for his generalization of the traditional concepts of acids and bases in which the base corresponded to an EPD and the acid to an electron-pair acceptor or EPA agent in Gutmann’s terminology (10).

In the 1950s the Lewis definitions were applied to the study of molecular charge-transfer complexes by Mulliken, who soon recognized that the source of the electron-pair provided by the donor molecule or EPD agent could correspond not only to a traditional nonbonding lone pair, in the Lewis-Sidgwick sense, but also to either a pi-bonding pair from a multiple bond or to a sigma bonding pair from a single bond – thus requiring that a distinction be made between traditional n-EPD species, on the one hand, and nontraditional π -EPD and σ -EPD species, on the other (11, 12). These distinctions have since been applied to more traditional

Lewis acid-base chemistry, to nucleophilic and electrophilic reactivity in organic chemistry, to Lewis base catalysis, and, of course, to the classification of ligands in coordination chemistry (9, 13-17).

It is very important that this electronic classification of ligands as various types of EPD agents or Lewis bases should not be confused with the conventional classification, found in virtually all advanced textbooks, of the complexes themselves as either σ -complexes or π -complexes or with talk of σ -bonding or π -bonding ligands, where the σ and π qualifiers refer to the nature of the metal-ligand bond in the final complex rather than to the source of the electron-pair in the isolated ligand (18).

In traditional coordination complexes, the ligands, whether monodentate or multidentate, function as n-EPDs. This means that the resulting metal-ligand bond corresponds to a conventional 2c-2e bond within the context of a localized bonding picture and this is what automatically determines the equality between the ACN and the EPCN. In contrast, the ligands in nontraditional organometallic complexes most often function as π -EPDs. This means that the resulting metal-ligand bond must be represented as a closed multicentered bonding component of some sort within the context of a localized bonding picture and this is what automatically determines that for these complexes $\text{ACN} > \text{EPCN}$.

Just as problems with steric hinderance may cause the denticity of a classical multidentate n-EPD ligand to vary from complex to complex, so with the hapticity of a π -EPD ligand. Thus in (1, 2, 4, 6- η^4 -cyclooctatetracene)(η^5 -cyclopentadienyl)cobalt(I) (LCN = 2, ACN = 9, EPCN = 5), the cyclooctatetracene ligand contributes four atoms to the ACN count and two electron pairs to the EPCN count, whereas in tricarbonyl-(η^6 -cyclooctatetracene)chromium(0) (LCN = 4, ACN = 9, EPCN = 6), it contributes six atoms to the ACN count and three electron pairs to the EPCN count. Likewise a given ligand may display alternative donor modes, depending on the complex in question. Thus N_2 functions as an n-EPD ligand when undergoing “end-on” coordination, as in the complex $(\text{NH}_3)_5\text{RuN}_2^{2+}$ (LCN = 6, ACN = 6, EPCN = 6). but as a π -EPD donor ligand when undergoing “edge-on” coordination, as in the N_2 -bridged complex $[\text{C}_5\text{Me}_5)_2\text{Sm}]_2\text{N}_2$ (LCN = 3, ACN = 12, EPCN = 7).

The cyclopentadienyl ligands in UCp_4 and ThCp_4 are obviously functioning as π -EPD agents, but what of the aminodiboranate ligands in the thorium complex reported by Daly *et al*? Since the hydrogen donor atoms on the ligands have no lone pairs and the B-H bonds have no multiple bond character, these ligands must be acting as σ -EPD agents. The quintessential example of a σ -EPD ligand involves the nonclassical edge-on

coordination of H_2 , as in the complex $ReH_5(H_2)(PPh_3)_2$ (LCN = 8, ACN = 9, EPCN = 8), in which the H_2 ligand interacts with the central ion via a closed 3c-2e bond within a localized bonding context. However, since the B-H bonds in the aminodiboranate ligands are interacting end-on with the Th^{4+} ion, this interaction must instead involve some sort of open multicentered bonding component when viewed from the context of a localized bonding picture. Though the exact details of this interaction would have to be worked out using a localization study and an appropriate localization function, such as the currently popular ELF approach, the question remains open as to whether it is appropriate to assume that each hydrogen atom is donating two electrons to the metal-ligand bonding when computing the resulting EPCN for thorium – whence our earlier use of the word “apparent” (19).

4. From the Octet Rule to a 32-Electron Rule?

This question of ligand electron counts brings us to our third and concluding point. Though the experimental structure of the crystalline $Th(H_3BNMe_2BH_3)_4$ complex indicates that one of the 16 possible hydrogen donor atoms on the four tetradentate aminodiboranate ligands is not significantly interacting with the Th^{4+} center, thereby reducing the total ACN from an idealized value of 16 to 15, quantum mechanical DFT calculations indicate that the idealized gas-phase complex should show a fully symmetrical ACN value of 16. Assuming each donor atom contributes a complete electron-pair, this would give the Th^{4+} center an EPCN = 16 and a valence electron count of 32 – a result which immediately raises the interesting question of whether this complex points to the possible existence of a 32-electron rule for inner-transition block elements paralleling the duplet rule for the H-He block, the octet rule for the main-block, and the 18-electron rule for the transition block (20, 21).

Most introductory chemistry textbooks continue to strenuously resist the replacement of valence-shell expansion structures for such hypervalent main-block species as SF_6 , PF_5 and SiF_6^{2-} with alternative octet structures employing 3c-4e, rather than traditional 2c-2e, bonds – though this alternative was suggested by Rundle and Pimentel more than 60 years ago and has since been repeatedly supported by quantum mechanical calculations (22, 23). These calculations imply that the octet rule represents a true upper limit on valence electron counts for the entire main-block, though one can envision that some compounds for elements occurring early in the block may fall short of this limit because steric hinderance prevents interaction with the proper number of ligands required for octet completion.

In such a case, we would have to distinguish between those species that are “electronically saturated” and have completed their octets versus those species which have become “sterically saturated” before achieving octet completion.

Though I am unaware of a significant number of cases in either the H-He block or the main-block where steric saturation inhibits either duplet or octet completion, the situation is quite different in the transition block because of its greater length. Electronically saturated organometallic complexes that obey the 18-electron rule are largely found among transition elements near the end of the block, whereas complexes for elements occurring early in the block generally achieve steric saturation long before they achieve shell completion. In addition, many organometallic textbooks also continue to list examples of “hypervalent” organometallic complexes which appear to have valence-electron counts great than 18 and include examples of apparent 19-, 20-, 21-, and 22-electron species (24).

However, analysis of these apparent hypervalent exceptions in terms of the splitting diagram for an octahedral field shows that these extra electrons are actually being assigned to the e_g^* orbitals, which are, in fact, antibonding in nature. Just as the occupation of both a bonding MO and its complementary antibonding MO, in the case of the main-block diatomics, converts these electrons into two lone pairs located at the outer periphery of the molecule in the corresponding localized Lewis diagram, so the occupancy of both the e_g and e_g^* orbitals converts the electrons in question into non-bonding electrons localized on the outer periphery of the surrounding ligands and actually reduces, rather than increases, the electron counts in the bonds surrounding the central atom. In this fashion the 18-electron rule is preserved as an effective upper limit for the transition metals. Indeed, this process has been illustrated in detail by Chu and Lee for the 20-electron tris(cyclopentadienyl)tungsten(IV) cation, $[WCp_3^+]$ (25).

When we move to the inner-transition block, we would expect, because of its even greater length, that electronically saturated 32-electron complexes would be even rarer and would only occur for elements at the very end of the block, with the compounds and complexes of most of the members of the block reaching steric saturation long before achieving shell completion. In keeping with this, many of the reported crown ether and cryptand complexes of the lanthanoids, though clearly showing valence-electron counts greater than 18, still fall short of achieving the theoretical upper limit of 32 (26). More recently, however, Pyykkö *et al* have reported calculations on a series of hypothetical 32-electron complexes involving the encapsulation of various actinoid atoms and cations within a multi-

dentate π -EPD C_{28} cage ligand (27), and both the solid-state and gas-phase structures of the $Th(H_3BNMe_2BH_3)_4$ complex reported by Daly *et al* should be viewed as a significant contribution toward the experimental realization of this promising goal – a contribution which is all the more remarkable because it involves an element (Th) which occurs so early in the f-block.

5. References and Notes

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