Mixed-Valent Compounds

Electron Cartography in Clusters

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Abstract: Deconvoluting the atom-specific electron density within polynuclear systems remains a challenge. A multiple-wavelength anomalous diffraction study on four clusters that share the same [Co₈Se₈] core was performed. Two cluster types were designed, one having a symmetric ligand sphere and the other having an asymmetric ligand sphere. It was found that in the neutral, asymmetric, CO-bound cluster, the Co–Co site is more highly oxidized than the other five Co atoms; when an electron is removed, the hole is distributed among the Se atoms. In the neutral, symmetric cluster, the Co atoms divide by electron population into two sets of three, each set being meridional; upon removal of an electron, the hole is distributed among all the Co atoms. This ligand-dependent tuning of the electron/hole distribution relates directly to the performance of clusters in biological and synthetic systems.

Herein, we detail how the electron density distribution within hexanuclear cobalt chalcogenide clusters is determined by systematically changing the nature of the substituents and the electron count. The foundations of reactivity in organic systems are predicated to a large extent on the electronic properties imparted to a substrate by its substituents. Thus, electron-withdrawing or electron-donating substituents will drastically alter the electron distribution within the molecule and, as a consequence, shut down or promote certain reactivity modes. By contrast, this level of predictability in reactivity is absent in molecules containing several metals in proximity, mainly because the electron distribution within polynuclear assemblies is not well understood. To investigate the oxidation levels of individual atoms within the cluster, we employed multiple-wavelength anomalous diffraction (MAD).[1] We chose [Co₈Se₈] cluster compounds because determining the individual atom valence for this cluster nucularity poses an unmet challenge in polynuclear synthetic systems. These molecules have a structure best described by a face-capped octahedron similar to those described by Cheveré et al.[2] Members of this family of materials are known to exhibit multivalency and superconductivity.[3] Because MAD relies on single-crystal data, this methodology allows us to study the relative valences of the individual atoms comprising the [Co₈Se₈] cluster core in two closely related metal chalcogenide compounds, namely [Co₈Se₈(CO)(PEt₃)] (1) and [Co₈Se₈(PBu₃)(PEt₃)] (2). We found that when the cluster core is asymmetrically substituted, as in the case of 1, the electron distribution follows what classical ligand field theory would predict for the case in which the Co–Co site is more electron deficient than the other five Co-PEt₃ sites. In contrast, when a symmetrical[4] all-phosphine ligand setting is imposed on the cluster core (2), the electron distribution remains asymmetrically grouped in a meridional fashion into two groups of three atoms, resembling the seam in a baseball. Furthermore, it is surprising that when 1 is oxidized the hole is delocalized on Se-based orbitals, whereas when 2 is oxidized the hole is taken up by the Co atoms. This reordering of the orbital energetics can be attributed directly to the CO and PBU₃ substituent or ligand effects on the [Co₈Se₈] cluster core. Most importantly, this study provides an atom-individual map of the electron distribution imposed by these ligand effects.

Mixed-valent polynuclear systems are ubiquitous in nature and also in synthetic materials.[5] They have unique properties resulting from the electronic and magnetic interaction of several metal atoms in close proximity.[6] Within those metal atoms, electron delocalization allows the cluster to distribute the electron density among the various redox-active centers.[7] As a consequence, determining the atom-individual valence of the sites involved in delocalization poses a formidable challenge. Despite the fundamental importance of the charge distribution in clusters, there have been only a few studies in which site-specific relative oxidation levels can be determined.[8] Moreover, until the present study, there has been no demonstration of how the electron density distribution is reconfigured upon oxidation at the atom-individual level within the same cluster framework.

The goal of the present study is to understand the following questions: 1) How is the atom site-specific electron density distribution modulated by systematically substituting a single ligand in polynuclear systems? 2) How is this electron density distribution reconfigured after the cluster undergoes oxidation? To answer these questions, we employed the cluster type [Co₈Se₈(L)(PEt₃)]⁺⁻ as prototypical example in which the ligand field around the cluster core [Co₈Se₈] can either be asymmetric (L = CO) or symmetric (L = PBU₃); in addition, these clusters can be investigated at two different formal electron counts (n = 0 or 1 + , see Figure 1). More specifically, the CO-bound asymmetric compound, [Co₈Se₈-
(CO)(PET₃)₃ (1, n = 0), has five Co atoms capped with PET₃ ligands while one is capped with CO (Figure 2a); meanwhile, the ligand sphere of the symmetric species, [Co₆Se₆(PBu₃)-PET₃]₆ (2, n = 0), has all six Co atoms capped with phosphines, one phosphine (tri-n-butylphosphine, PBU₃) of which is different from the others to maintain the overall low symmetry of the molecule (Figure 2b). In addition, to explore the electron density reconfiguration after oxidation, the one-electron oxidized compounds [Co₆Se₆(CO)(PET₃)]₆[PFl₆] (1- [PF₆]ₖ, n = 1 +) and [Co₆Se₆(PBu₃)(PET₃)]₆[PFl₆] (2- [PF₆]ₖ, n = 1 +) were also investigated (Figure 2c,d).

The synthesis of 1 and 1- [PF₆]ₖ has been previously reported.[5] Following the same photochemical protocol, 2 and 2- [PF₆]ₖ were synthesized by substitution of the CO in 1 and 1- [PF₆]ₖ with PBU₃. High-quality single crystals of the neutral species 1 and 2 were obtained by vapor diffusion of diethyl ether and pentane into toluene, respectively (Figure 2e,f). Similarly, crystals of 1- [PF₆]ₖ and 2- [PF₆]ₖ were grown by diffusing Et₂O into a concentrated solution of the clusters in dichloromethane (Supporting Information, Figures S5 and S6).[10] The cluster core structure [Co₆Se₆] in all four species has a geometry best described by an ideal face-capped octahedron, in which the Se atoms occupy the vertices of a cube and the Co atoms reside in the center of each of the cube’s faces.

Compounds 1 and 2 have an electron count that results in a formal mixed-valent configuration [4CoII2CoIII] (assuming all selenium atoms as Se²⁻), and thus 1- [PF₆]ₖ and 2- [PF₆]ₖ have [5CoIICoIV]²⁻. Consequently, all four species contain itinerant electrons delocalized within the [Co₆Se₆] core. This electron sharing can be quantified by extracting the proportionality constant K of each species by means of cyclic voltammetry.[12] In this regard, the K values obtained for the neutral species (1, 1.3 × 10⁻¹⁴ and 2, 8.3 × 10⁻¹⁵), which are higher than those of the charged clusters in 1- [PF₆]ₖ (5.3 × 10⁻¹⁰) and 2- [PF₆]ₖ (6.1 × 10⁻¹⁷), indicate an overall large degree of electron delocalization (Supporting Information, Table S3). To highlight this point, we can compare these K values to well-established strongly delocalized compounds having K values of circa 10³, for example, the Creutz-Taube ion.[13] While the electrochemical data presents an overall picture indicating a large extent of electron sharing within the polynuclear assembly, it does not provide much insight into the electron density environments of the individual atoms. Therefore, to dissect the site-specific relative electron densities for each atom in the [Co₆Se₆] cluster core, we have examined the wavelength dependence of the atomic scattering factors on high-quality single crystals of 1, 1- [PF₆]ₖ, 2, and 2- [PF₆]ₖ.

Valence differentiation studies, for example, determination of Cu oxidation state in the superconductor YBa₂Cu₃Oₓ,[84] make use of the large variation of the atomic scattering factor f of an atom around an absorption edge, which is given by f = f₀ + f' + if'', where f₀ is the
scattering factor of the unperturbed atom, and $f'$ and $f''$ correspond to the contributions from the in-phase and out-of-phase components of the anomalous scattering, respectively. MAD has been utilized extensively in polycrystalline systems, but less so in single crystal studies. In reports of MAD on single crystals, the mixed-valent species under study displays a clear minimum in the $f'$ versus energy curve for each atom site, which indicates the edge position, thus allowing a clear assignment of the relative oxidation states of the redox atoms involved in electron sharing. Moreover, as electron delocalization increases this assignment becomes less straightforward.

The MAD experiments in this report were carried out after first determining the Co and Se K-edge positions on the same single crystal to be further examined by X-ray diffraction (top part of Figure 3e–h). With this information, we designed a data collection strategy that consists of collecting partial diffraction data (720 frames) every 1 eV from below the pre-edge feature covering the entire K-edge and until right after the edge; additionally, below the pre-edge and above the edge, data was collected every 3–5 eV (see Supporting Information). Moreover, prior to collecting the partial diffraction data sets, the full structure was determined at high energy (30 keV). All the structure parameters from

Figure 3. Truncated molecular structures of a) 1, b) 2, c) 1[PF$_6$], and d) 2[PF$_6$]. Insets (a–d): Relative oxidation levels within the [Co$_6$Se$_8$] core, where a Co red sphere indicates a higher oxidation level relative to the blue ones, and similarly a Se yellow sphere indicates a higher oxidation level relative to the gray ones. e–h) Data plots from 1 (circles), 2 (squares), 1[PF$_6$] (diamonds), and 2[PF$_6$] (triangles). In each panel the top curve corresponds to the single-crystal X-ray fluorescence scan collected around the Co K-edge in steps of 1 eV at 100 K on the same crystal employed in all the diffraction data. The bottom part of each panel corresponds to the anomalous scattering factor $f'$ of each cobalt center in the [Co$_6$Se$_8$] cluster core. The anomalous scattering data was refined using the full structure data set for each compound collected at 30 keV as the reference.
the 30 keV data were used and kept fixed when refining the partial diffraction data except for $f'$ and $f''$ for every Co and Se atom at the Co and Se K-edge, respectively. In this manner, and since every Co and Se atom in 1, 1[PF$_6$]$_3$, 2, and 2[PF$_6$]$_3$ are crystallographically independent, we were able to deconvolute the individual $f'$ and $f''$ curves for all atoms within the [Co$_2$Se$_6$]$_3$ cluster cores.$^{[14]}$

In Figure 3a–d we display truncated structures of all four species with the corresponding atom labels subsequently used in the anomalous scattering plots in Figure 3e–h. The anomalous scattering plots in Figure 3e–h provide the full picture of the $f'$ evolution around the absorption edge. Regardless of the substitution pattern and oxidation level, all four species display a pre-edge feature in the Co K-edge at 7704 eV (insets in Figure 3e–h). The anomalous scattering $f'$ curve for 1 is shown in Figure 3e (bottom). Starting at low energy, all Co sites have superimposable $f'$ values. After the minimum, which occurs around 7711 eV, all Co sites remain equivalent within experimental error, except Co1. This site's $f'$ curve broadens and departs from the rest in the high-energy side indicating an overall higher oxidation level than the other five cobalt sites, exemplified in Figure 3a, inset. While the Co oxidation states can be described formally as $[4Co^{II}2Co^{III}]$, the experimental data does not support this, showing that Co1 has a slightly higher oxidation level than Co2 to Co6, which share the same valence. This result fits with chemical intuition, by which one expects the CO-bound Co site to be more electron deficient than the other, phosphine-bound, sites. The resulting electron density at the Co centers correlates directly with the donor–acceptor properties of CO and PEt$_3$. For instance, CO withdraws electron density since it acts as a weak $\sigma$-donor and strong $\pi$-acceptor, whereas alkylphosphines are known as strong $\pi$-acceptors.$^{[17]}$ Remarkably, the electron density distribution changes considerably in the symmetric all phosphine-bound species 2, in which two overall oxidation levels are observed in a meridional arrangement (Figure 3b, inset) formed by Co1, Co3, and Co5 residing at a higher valence relative to Co2, Co4, and Co6 (Figure 3f). In terms of the Se local environments, $^{[7]}$Se NMR data shows two and one (broad) chemical environments in 1 and 2, respectively (Supporting Information, Figure S7).

We examine the $f'$ anomalous scattering data extracted from 1[PF$_6$]$_3$ and note that it is identical within experimental error to that of 1 (Figure 3g). This is remarkable since 1[PF$_6$]$_3$ has one electron less than 1. Hence, the hole in 1[PF$_6$]$_3$ does not sit on the Co atoms. We hypothesize the Se atoms in 1[PF$_6$]$_3$ are oxidized and no longer display a unique valence as in the parent compound 1 (Figure 3c, inset). Unfortunately, the refined data at the Se K-edge for 1[PF$_6$]$_3$ (Supporting Information, Figure S14) is lower in quality than that of 1. In contrast, the MAD analysis on 2[PF$_6$]$_3$ shows coalescence of the Co environments into a single one. Remarkably, the burden of oxidation at Co falls now upon all six Co atoms as seen in Figure 3h and exemplified in the inset of Figure 3d.

Figure 4 displays the electron density evolution from 1 to 1[PF$_6$]$_3$ and from 2 to 2[PF$_6$]$_3$. The scattering factors, $f'$, of 1 and 1[PF$_6$]$_3$ are compared across a small energy window (7710–7718 eV), in which the departure of Co1 (CO-bound site) from the rest is apparent (Figure 4a,b). The behavior is different in 2 and 2[PF$_6$]$_3$, in which the meridional arrangement of two sets of three Co atoms each, described above for 2, is lost and now all Co atoms in 2[PF$_6$]$_3$ reside at the same oxidation level (Figure 4c,d). Thus, triggered by oxidation, the binomial distribution of oxidation levels in 2 merges into a single level in 2[PF$_6$]$_3$ that resides right in between the former oxidation levels seen in 2 (Supporting Information, Figure S18).

At a first glance the charge distribution obtained from MAD analysis is contradictory with the overall reduction in $\pi$-backbonding observed towards CO and the phosphines.$^{[17]}$ We took a closer look at the bond metrics within each oxidation sequence. In the sequence of 1 to 1[PF$_6$]$_3$ the Co–CO and Co–P$_{avg}$ bond distances indicate an overall decrease in $\pi$-backbonding by changing from 1.728(5) to 1.740(5) Å, and from 2.142(2) to 2.180(3) Å, respectively. Similarly, the CO stretching frequency ($\nu_{CO}$) is in line with the decreased $\pi$-backbonding upon oxidation by going from 1958 to 1983 cm$^{-1}$.$^{[9]}$ At the same time the Co–Se$_{avg}$ distances in 1 and 1[PF$_6$]$_3$ remain unchanged (Table S2). While this alone would indicate an overall increase in oxidation of all Co centers, it appears that the electron density directed towards $\pi$-backbonding with the peripheral ligands is now used to enhance intrACLuster bonding judged by an overall contraction of the Co–CO$_{avg}$ distances in 1 (2.946(5) Å) and 1[PF$_6$]$_3$ (2.906(11) Å). We thus conclude that these two effects level each other and gives support to the electron density distribution obtained from MAD. In agreement, the sequence from 2 to 2[PF$_6$]$_3$ displays an overall expansion of the Co–P$_{avg}$ (2, 2.141(1) Å; 2[PF$_6$]$_3$, 2.176(1) Å) and contraction of the Co–Co$_{avg}$ (2, 2.953(4) Å; 2[PF$_6$]$_3$, 2.921(10) Å) distances.

The electron density redistribution seen in 1, 2, 1[PF$_6$]$_3$, and 2[PF$_6$]$_3$ is remarkable and points to an electronic structure change upon a minor perturbation of the ligation pattern.
While metal-based redox is usually invoked, the data presented herein demonstrates that when removing an electron from the CO-bound species 1, the oxidation burden rests primarily at the chalcogen, Se atoms, similar to what is observed in biological cofactors. In contrast, removal of an electron in the ligand field symmetric all-phosphine species 2 leaves behind a hole delocalized primarily within the metal atoms (Co). Thus, by deconvoluting the individual relative oxidation levels in polynuclear systems through MAD, we were able to map the electron density configuration within an unsymmetrical (as in 1, 1[PF$_6$]) and symmetrical (as in 2, 2[PF$_6$]) ligand field environment. Furthermore, we were able to determine how the electron density map is reconfigured upon oxidation. This study demonstrates the important effect a single ligand has on the electron density distribution within a polynuclear system akin to the electron withdrawing/donating effect of substituents in organic systems. These results also indicate that while a first-order, electron-counting description of the electronic structure of such clusters may be useful and valuable, the details of chemical bonding within the clusters is clearly much more complex.

This ligand-dependent tuning of the electron/hole reservoirs has direct relevance to how biological cofactors function in which similar mechanisms are likely in play when biological polynuclear systems bind and activate substrates (e.g. N$_2$, H$_2$O, CO$_2$, or CH$_4$), especially those comprising multiple metal atoms acting in concert. Moreover, this tuning of the electron density distribution based on the peripheral ligand field should have important implications towards building magnetic anisotropy in magnetic materials or defining preferred conduction pathways in superconductors. The results on these complex clusters present an ideal system to explore for those at the forefront of quantum chemical calculations. Future studies exploring the electron density distribution across different overall oxidation levels in biological cofactors and materials will yield insight into the mechanism of action of these systems.

Acknowledgements


Conflict of interest

The authors declare no conflict of interest.

Keywords: clusters · electron density distribution · mixed-valent compounds · multiple-wavelength anomalous diffraction

How to cite: Angew. Chem. Int. Ed. 2018, 57, 13815–13820

4) We use tri-n-butylphosphine (P’Bu$_3$) as the closest relative of triethylphosphine (PEt$_3$) that gives high quality crystals while inverting a version center in the cluster. Thus, we justify the wording “symmetrical all-phosphine ligand setting”, since the ligand field imposed by P’Bu$_3$ is very similar to PEt$_3$ and different from the asymmetric environment caused by the largely distinct CO ligand.
10) CCDC 1565550 (1), 1565552 (1[PF$_6$]), 1565551 (2), and 1565553 (2[PF$_6$]) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.
11) [Co$_n$]$^+$ [Co$_n$]$^{3+}$ [Co$_n$]$^{4+}$, where the equilibrium constant is referred to as the comproportionation constant (K$_c$).
We note that near the absorption edge, the anomalous scattering factors are more accurately described as second-rank tensors that interact with the polarization of the X-ray beam (L. K. Templeton, D. H. Templeton, Acta Crystallogr. Sect. A 1988, 44, 1045–1051). In this work, the polarization dependence is largely averaged out in the final refinement because we collected 180° q scans with the q axis parallel to the plane of polarization. As a future improvement, a full refinement of three-dimensional anomalous scattering factors would contain valuable chemical information, especially in the pre-edge region where symmetry-allowed electronic transitions are a significant part of the absorption coefficient. We thank two anonymous reviewers for helpful comments on this subject.

Manuscript received: June 4, 2018
Accepted manuscript online: September 4, 2018
Version of record online: September 21, 2018