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Mendeleev Commun., 2022, **32**, 202–204

Mendeleev Communications

Decision problem with high residual electron density on the metal atom

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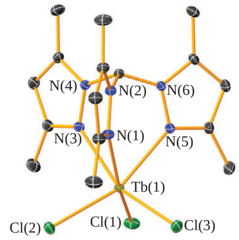
DOI: 10.1016/j.mencom.2022.03.016

It is shown that replacing the experimental electron density with the theoretical one on the terbium atom describes the experimental topology in the coordination sphere with high accuracy. Such a replacement is fundamentally important in the case of high residual electron density on a heavy metal atom.



Keywords: high-resolution X-ray diffraction, experimental charge density, experimental–theoretical charge density, terbium atomic invariom, neutral terbium(III) complex, tris(3,5-dimethyl-1-pyrazolyl)methane, single-molecule magnets.

The study of experimental electron density (ED) topology plays an important role in modern chemical science.[1–5] The study of the ED distribution requires highly reflective crystals, which cannot always be obtained. Therefore, experimental–theoretical approaches based on atomic,[6–17] molecular[18–22] and crystal[23] invarioms (aspherical scattering factors for atom, molecule and asymmetric unit cell, respectively) are widely used to investigate the ED topology. The electronic characteristics of atoms [populations of the spherically symmetric valence shell (P_{val}), multipole parameters (P_{lm}) describing its deformation, the corresponding expansion–contraction coefficients (k, k')] are calculated in these approaches based on theoretical structural amplitudes. The advantage of these approaches is that they do not require high-resolution X-ray diffraction experiments. Indeed, these approaches have proven to be reliable tools for studying ED topology on different classes of compounds.[8–23] Consequently, the time-consuming step of obtaining highly reflective crystals is eliminated.

However, what to do if a high-resolution experiment has already been carried out, and in the process of multipole refinement, a high residual ED on metal atoms is observed. Such a situation usually takes place in coordination and organometallic compounds containing 'heavy' metal atoms. The reason for the high residual ED on metal atoms can be difficulties associated with the correct accounting for absorption, inelastic scattering of X-rays by electrons of the crystal lattice and also extinction phenomenon. In our high-resolution data, the residual ED on heavy metal atoms (Sb, Pb, Ln) can reach up to 10 e Å^{-3}. Obviously, such data cannot be published since the electronic parameters of metal atoms (P_{val}, P_{lm}, k, k') in the multipole refinement may assume unrealistic values. As a result, the topological characteristics of the ED in the coordination sphere of a metal atom may be incorrect. In such cases, we propose to theoretically calculate the electronic characteristics of the metal atom (P_{val}, P_{lm}, k, k'; atomic invariom) for a specific coordination sphere. The electronic characteristics of other atoms are refined from high-resolution experimental data. It should be noted that the electronic parameters of the metal atom obtained in this way are not refined. Therefore, the high residual ED on the metal atom cannot affect them.

Thus, the purpose of this work is to compare the topological characteristics of the ED in the coordination sphere of a metal atom, obtained by experimental and experimental–theoretical methods, using the example of terbium trichloride coordinated by neutral tris(3,5-dimethyl-1-pyrazolyl)methane (Tpm). From a chemical point of view, interest in this class of complexes is because they are mononuclear single-molecule magnets.[24]

The synthesis and routine structure of terbium trichloride coordinated by the neutral Tpm ligand, [Tb(Tpm)Cl_3]·2MeCN $\mathbf{1_{exp}}$, have been published previously[24] [Figure 1(*a*)], while the high-resolution X-ray diffraction data are discussed in this work for structures $\mathbf{1_{iam}}$ (independent atoms model) and $\mathbf{1_{exp}}$ (multipole refinement).[†]

[†] The data were collected on a Bruker D8 Quest diffractometer for $\mathbf{1_{iam}}$ (graphite-monochromated MoKα radiation) at 100 K. The structure was solved by dual methods and refined on F^2 using the SHELXTL package.[25] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined in the riding model. SADABS[26] was used to perform area-detector scaling and absorption corrections.

Crystal data for $\mathbf{1_{iam}}$. M = 645.77, monoclinic, space group $P2_1/n$, a = 9.5240(4), b = 16.2801(7) and c = 17.1403(8) Å, β = 94.2690(10)°, V = 2650.3(2) Å^3, Z = 4, d_{calc} = 1.618 Mg m^{-3}, μ = 2.994 mm^{-1}, F(000) = 1280. Intensities of 564020 reflections were measured (θ < 53.907°) and 32563 independent reflections [R_{int} = 0.0381] were used in further refinement. For $\mathbf{1_{iam}}$ the refinement converged to wR_2 = 0.0590 and goodness of fit GOF = 1.050 for all observed reflections [R_1 = 0.0245 was calculated against F for 30986 observed reflections with $I > 2\sigma(I)$]. Largest diff. electron density, peak/hole: 2.217 / –5.581 e Å^{-3}.

The multipole refinement was carried out within the Hansen–Coppens formalism[27] using the MoPro program package.[28] Before the refinement, C–H bond distances were normalized to the values obtained in neutron diffraction analyses.[29] The levels of the multipole expansion were hexadecapole for the terbium atom, octupole for all other non-hydrogen atoms and one dipole for hydrogen atoms.

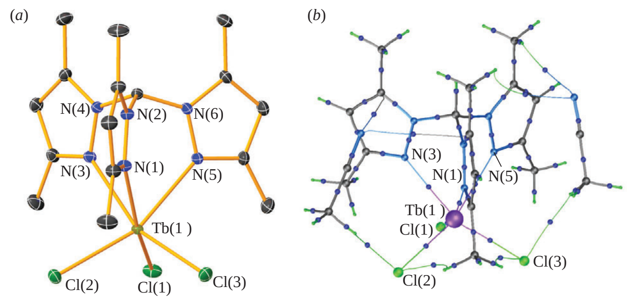


Figure 1 (*a*) Molecular structure[24] and (*b*) experimental molecular graph of complex $\mathbf{1_{exp}}$. The critical points CP(3,–1) are presented by blue points. Thermal ellipsoids are drawn at 50% probability level.

Analysis of the residual ED obtained in structure $\mathbf{1_{iam}}$ has shown that the maximum peak is near atom C(5) and equal to 2.22 e Å^{-3} (Figure S1, see Online Supplementary Materials). In the process of multipole refinement, this peak does not decrease (2.12 e Å^{-3}). This residual ED is located far from the terbium atom and does not affect its electronic parameters during multipole refinement. We believe that this residual ED is caused by the interference of the incident and diffracted X-rays. Two residual ED peaks (1.74 and 1.81 e Å^{-3}) in structure $\mathbf{1_{iam}}$ were detected near the terbium atom (see Figure S1). The multipole refinement significantly reduces the residual ED, which does not exceed ~0.4 e Å^{-3} near the terbium atom (Figure S2). Obviously, this lowering of the residual ED on the metal atom is because the multipole refinement model is better than the IAM model. It should be noted that the electronic characteristics of the terbium atom in structure $\mathbf{1_{exp}}$ were refined without any restrictions. We believe that the topological characteristics of the ED in the coordination sphere of terbium in structure $\mathbf{1_{exp}}$ are as correct as possible and can be adequately compared with those in structure $\mathbf{1_{Tb\text{-}inv}}$ (Tables 1–3).

The main distances to the critical points (3,–1) [CP(3,–1)] and their curvature (λ) in the coordination sphere of the Tb atom, obtained experimentally (structure $\mathbf{1_{exp}}$) and experimentally–theoretically (structure $\mathbf{1_{Tb\text{-}inv}}$), are presented in Table 1. As one can see, the distances to CP(3,–1) in structures $\mathbf{1_{exp}}$ and $\mathbf{1_{Tb\text{-}inv}}$ are almost the same. In addition, the curvature of the ED at these points perfectly coincides with each other. The largest difference between the λ values is observed for the λ_3 value at the Tb(1)–N(5) bond and is ~3%. The experimental and experimental–theoretical molecular graphs in structures $\mathbf{1_{exp}}$ and $\mathbf{1_{Tb\text{-}inv}}$ also coincide [Figures 1(*b*) and S10]. The almost exact coincidence of the ED curvature at CP(3,–1) between structures $\mathbf{1_{exp}}$ and $\mathbf{1_{Tb\text{-}inv}}$ allows us to assume that other topological characteristics will also be the same. As shown in Table 2, the main topological characteristics of the ED in the coordination sphere of the terbium atom in complexes $\mathbf{1_{exp}}$ and $\mathbf{1_{Tb\text{-}inv}}$ coincide with each other except for the local density values of electron energy [h_e(r)]. However, the signs of the experimental and experimental–theoretical values of h_e(r) are the same. Thus, the experimental–theoretical topology of the ED in structure $\mathbf{1_{Tb\text{-}inv}}$ reliably reproduces the experimental one, despite the fact that the residual ED near the terbium atom in structure $\mathbf{1_{Tb\text{-}inv}}$ is ~1.5 e Å^{-3} (Figure S3).

The topological experimental atomic charge on the terbium atom in structure $\mathbf{1_{exp}}$ is 1.38 e and differs from the experimental–theoretical charge by ~11% (1.53 e). In turn, the volumes of the terbium atom are almost identical (20.50 Å^3 in structure $\mathbf{1_{exp}}$ and 20.48 Å^3 in structure $\mathbf{1_{Tb\text{-}inv}}$). It should be noted that the

Table 1 Main distances from the Tb atom to CP(3,–1) (D_1) and from CP(3,–1) to the Cl or N atom (D_2), as well as their curvature (λ_1, λ_2, λ_3) in the coordination sphere of the Tb atom obtained experimentally (structure $\mathbf{1_{exp}}$) and experimentally–theoretically (structure $\mathbf{1_{Tb\text{-}inv}}$).

Bond	Structure	D_1/Å	D_2/Å	λ_1 (a.u.)	λ_2 (a.u.)	λ_3 (a.u.)
Tb(1)–Cl(1)	$\mathbf{1_{exp}}$	1.311	1.258	–0.041	–0.041	0.263
	$\mathbf{1_{Tb\text{-}inv}}$	1.310	1.259	–0.042	–0.041	0.267
Tb(1)–Cl(2)	$\mathbf{1_{exp}}$	1.314	1.262	–0.041	–0.040	0.258
	$\mathbf{1_{Tb\text{-}inv}}$	1.314	1.263	–0.042	–0.040	0.261
Tb(1)–Cl(3)	$\mathbf{1_{exp}}$	1.313	1.261	–0.041	–0.041	0.260
	$\mathbf{1_{Tb\text{-}inv}}$	1.312	1.261	–0.042	–0.040	0.264
Tb(1)–N(1)	$\mathbf{1_{exp}}$	1.292	1.185	–0.053	–0.050	0.302
	$\mathbf{1_{Tb\text{-}inv}}$	1.291	1.186	–0.054	–0.050	0.301
Tb(1)–N(3)	$\mathbf{1_{exp}}$	1.302	1.196	–0.050	–0.047	0.289
	$\mathbf{1_{Tb\text{-}inv}}$	1.300	1.197	–0.050	–0.047	0.286
Tb(1)–N(5)	$\mathbf{1_{exp}}$	1.297	1.190	–0.051	–0.049	0.295
	$\mathbf{1_{Tb\text{-}inv}}$	1.296	1.192	–0.052	–0.049	0.286

The refinement of compound $\mathbf{1_{exp}}$ (θ < 51.42°) was carried out against F and converged to R = 0.0224, wR = 0.0225, GOF = 0.994 for 28022 merged reflections with $I > 0\sigma(I)$. The ratio of the number of reflections to the number of refined parameters was > 10 for $\mathbf{1_{exp}}$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria.[30] The topology of experimental ρ(r) function was analyzed using the WinXPRO program package.[31] The residual electron densities around the terbium atom were not greater than ~0.4 e Å^{-3}, largest diff. electron density, peak/hole: 2.12 / –5.64 e Å^{-3} for $\mathbf{1_{exp}}$.

CCDC 2103038 and 2103039 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Table 2 The main distances and topological parameters of the ED in the coordination sphere of the Tb atom obtained experimentally (structure $\mathbf{1_{exp}}$) and experimentally–theoretically (structure $\mathbf{1_{Tb\text{-}inv}}$).

Bond	Structure	d/Å	ν(r)[a] (a.u.)	ρ(r)[a] (a.u.)	$\nabla^2\rho$(r)[a] (a.u.)	h_e(r)[a] (a.u.)
Tb(1)–Cl(1)	$\mathbf{1_{exp}}$	2.5688(2)	–0.047	0.045	0.181	–0.0009
	$\mathbf{1_{Tb\text{-}inv}}$	2.5687(2)	–0.047	0.044	0.183	–0.0007
Tb(1)–Cl(2)	$\mathbf{1_{exp}}$	2.5764(2)	–0.046	0.044	0.177	–0.0008
	$\mathbf{1_{Tb\text{-}inv}}$	2.5763(2)	–0.046	0.044	0.180	–0.0005
Tb(1)–Cl(3)	$\mathbf{1_{exp}}$	2.5733(2)	–0.047	0.044	0.179	–0.0009
	$\mathbf{1_{Tb\text{-}inv}}$	2.5732(2)	–0.047	0.044	0.181	–0.0006
Tb(1)–N(1)	$\mathbf{1_{exp}}$	2.4770(5)	–0.053	0.048	0.199	–0.002
	$\mathbf{1_{Tb\text{-}inv}}$	2.4771(6)	–0.053	0.048	0.197	–0.002
Tb(1)–N(3)	$\mathbf{1_{exp}}$	2.4971(6)	–0.050	0.046	0.191	–0.001
	$\mathbf{1_{Tb\text{-}inv}}$	2.4969(6)	–0.050	0.046	0.188	–0.001
Tb(1)–N(5)	$\mathbf{1_{exp}}$	2.4875(5)	–0.052	0.047	0.195	–0.001
	$\mathbf{1_{Tb\text{-}inv}}$	2.4875(6)	–0.051	0.047	0.193	–0.002

[a] The values of the local density of potential energy ν(r), the total ED ρ(r), its Laplacian $\nabla^2\rho$(r) and the local density of electronic energy h_e(r) are shown at CP(3,–1) of the bond.

Table 3 Number and energy of intermolecular contacts in structures $\mathbf{1_{exp}}$ and $\mathbf{1_{Tb\text{-}inv}}$.[a]

Contacts	$\mathbf{1_{exp}}$			$\mathbf{1_{Tb\text{-}inv}}$		
	Number of contacts	Energy range of individual contacts/ kcal mol^{-1}	Total contact energy/ kcal mol^{-1}	Number of contacts	Energy range of individual contacts/ kcal mol^{-1}	Total contact energy/ kcal mol^{-1}
Cl···H	15	0.2–1.2	11.4	15	0.2–1.3	11.9
N···H	8	0.3–1.5	5.8	8	0.3–1.5	6.1
C···N	2	0.9–1.2	3.1	2	1.0, 1.3	
C···H	7	0.5–0.9	5.2	7	0.5–0.9	5.0
H···H	2	0.4	0.8	3	0.4	1.6
C···C	1	1.1		1	1.2	
	Lattice energy/kcal mol^{-1} 27.4			Lattice energy/kcal mol^{-1} 28.1		

[a] The energy of intermolecular interactions was calculated according to the EML correlation [E = 313.76ν(r), kcal mol^{-1}].[32]

experimental–theoretical charges on metal atoms are always more electropositive than the experimental ones.[18–20] The theoretically calculated ED of the terbium atom should not significantly affect the architecture and energy of intermolecular interactions. However, we have tested the possibility of such an influence.

As can be seen from Table 3, complex $\mathbf{1}_{\mathbf{Tb\text{-}inv}}$ exactly reproduces all intermolecular interactions, except for H···H ones, in complex $\mathbf{1}_{\mathbf{exp}}$. Thus, the theoretical ED of the terbium atom does not significantly affect the architecture and energy of intermolecular contacts. From a practical point of view, the energies of intermolecular interactions in complexes $\mathbf{1}_{\mathbf{exp}}$ and $\mathbf{1}_{\mathbf{Tb\text{-}inv}}$ are the same.

In this work, we have shown that replacing the experimental ED on the terbium atom with the theoretical one (the atomic invariom) has no significant effect on the topological characteristics of the ED in the coordination sphere and on the energy of intermolecular interactions. Consequently, such a replacement is important for complexes containing ‘heavy’ metal atoms on which a high residual ED remains. This approach is possible primarily because the theoretical atomic parameters (atomic invariom) of the ‘heavy’ metal atom are not refined in the multipole refinement process. Therefore, the high residual ED does not affect them. Thus, using this approach will make it possible to avoid difficulties with a high residual density on the ‘heavy’ metal atom in high-resolution experiments.

This work was supported by the Russian Science Foundation (project no. 21-13-00336). The study was carried out using the equipment of the center for collective use ‘Analytical Center of the IOMC RAS’ with the financial support of the grant ‘Ensuring the development of the material and technical infrastructure of the centers for collective use of scientific equipment’ from the Ministry of Science and Higher Education of the Russian Federation (unique project identifier is RF2296.61321X0017, Agreement with the G. A. Razuvaev Institute of Organometallic Chemistry RAS no. 075-15-2021-670).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.016.

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Received: 16th August 2021; Com. 21/6644