ABSTRACT: Mg$_{29-x}$Pt$_{4+y}$ represents the family of complex intermetallic compounds (complex metallic alloys, CMAs). It crystallizes in the cubic non-centrosymmetric space group F43m with $a = 20.1068(2)$ Å and around 400 atoms in a predominantly ordered arrangement. The local disorder around the unit cell origin is experimentally resolved by single-crystal X-ray diffraction in combination with atomic-resolution transmission electron microscopy (TEM, high-angle dark-field scanning TEM) studies. The quantum theory of atoms in molecules-based analysis of atomic charges shows that the unusual mixed Mg/Pt site occupation around the origin results from local charge equilibration in this region of the crystal structure. Chemical bonding analysis reveals for Mg$_{29-x}$Pt$_{4+y}$—rather unexpected for a crystal structure of this size—space-separated regions of hetero- and homoatomic bonds involving three to six partners (bonding inhomogeneity). Pt-containing 11- and 13-atomic units formed by heteroatomic 3a-, 4a-, and 5a-bonds are condensed via edges and faces to large super-tetrahedrons, which are interlinked by Mg-only 6a-bonds. Spatial separation of the regions with different bonding features is the key difference between the title compound and other CMAs, which are characterized by a predominantly homogeneous distribution of heteroatomic bonds.

1. INTRODUCTION

The chemistry which underlies intermetallic compounds is one of the most complex topics in the field of materials science, mainly because of their broad range of structures, nature of the elements involved, bonding peculiarities, and physical properties. In a previous study, Pauling had already considered the understanding of the bonding mechanisms, which stabilize intermetallic crystal structures, as a special challenge for structural chemistry. Among this family of inorganic materials, a special category is represented by complex intermetallic compounds (earlier often called complex metallic alloys, CMAs). As their characteristic features were considered giant units, cluster arrangement of atoms with a high number of different atomic environments, where icosahedral coordination plays a prominent role, and inherent disorder—configurational, chemical, or substitutional—with partial site occupancy and split positions. A CMA can show large periodic structures with hundreds or thousands of atoms in the unit cell (like Ta$_{306}$Al$_{1282}$Cu$_{244.04}$, Pearson symbol: cF23134u21610) and—at least in the current state of investigations—with a higher frequency of occurrence for binary compounds rather than for ternary compounds.

A common strategy to describe a CMA from a geometric point of view is the grouping of atoms into local atomic arrangements (crystallographic clusters), which makes the crystal structure easier to visualize, perceive, and understand the geometric organization; it reduces the degree of complexity and allows one to relate the CMA to simpler crystal structures. This is the nested polyhedral unit approach, which was introduced first for the description of the γ-brass structure. The choice of a crystallographic cluster is considered as reasonable, if its shells are as spherical as possible and are quite separate with respect to the distances between the shells and with respect to the center of the nested polyhedrons. On the other hand, the so-defined crystallographic clusters are not in agreement with the chemical definition of such an entity, as the chemical definition entails atomic interactions within the chemical clusters that are stronger than the interaction of the clusters with neighboring aggregates. Thus, it would be preferable to raise the question about the stabilization mechanisms for these structural units. Based on the intensive studies of crystal structures and electronic configurations of γ-brass phases, the theory of electronic stabilization for metallic materials, known as Hume-Rothery rules, was developed. These rules, which are usually applied for explaining the stability of CMA, assume a rather homogeneous bonding caused by multi-atomic inter-
actions (metallic bond). Quantum chemical investigations of chemical bonding in CMA are naturally hindered by the huge size of the unit cells and inherent disorder. Thus, the role of the charge transfer in the stabilization was only recently pointed out for an example of the ordered CMA Be$_2$Pt$_5$ and its chemically analogous but non-complex Be$_2$Pt. Most of the CMA with approx. 400 atoms in the unit cell crystallize in the face-centered cubic Bravais lattice, and—in particular—36 of them crystallize with the space group $I4/3m$ (no. 216). Mg-rich transition-metal compounds already reported in the literature$^{22-25}$ can also be considered as CMA since all of them fulfill the conditions mentioned above. In the Mg–Pt system, the possibility of the existence of a Mg-rich phase with the composition Mg$_5$Pt, similar to that of Mg$_5$Pd, was reported already in the 1960s without further details.$^{24,25,28}$ The here-presented joint study of the crystal structure based on single-crystal X-ray diffraction (XRD), together with a transmission electron microscopy (TEM) investigation, and analysis of the chemical bonding with the position-space approach sheds light on the interplay of chemical bonding and partial crystallographic disorder in the title compound.

### 2. EXPERIMENTAL SECTION

Samples with nominal compositions Mg$_5$Pt and Mg$_9$Pt were prepared from elemental Mg (granules; Alfa Aesar, 99.98%) and Pt (powder; Alfa Aesar, 99.9%). Pt powder was added on the already induction-melted Mg granules on the bottom of a tantalum tube. The tantalum tube was welded and heated up to 1080 °C in a high-frequency furnace for about 5 min. The melted product was ground and compacted into a pellet, and the latter was placed in an alumina crucible and sealed into a tantalum tube for the annealing procedure. The sample after being cooled from 650 to 530 °C in 240 h was held at this temperature for 5 days. The reaction product consisted of a polycrystalline compacted gray pellet with a metallic appearance. The complete sample preparation was performed in an argon (Ar)-filled glovebox (MBraun, $p$(H$_2$O)/O$_2$) < 0.1 ppm).

The study of the thermal behavior of Mg$_{29−x}$Pt$_{4+y}$ was carried out on a Netzsch DSC 404C Pegasus differential scanning calorimeter in a flowing Ar atmosphere (99.999%, 100 mL/min) with subsequent drying and oxygen post-purification via a Big Oxygen Trap (Trigon). The measurements were made with a Netzsch DSC 404C Pegasus differential scanning calorimeter in a flowing Ar atmosphere (99.999%, 100 mL/min) with subsequent drying and oxygen post-purification via a Big Oxygen Trap (Trigon). The measurements were determined with wavelength-dispersive X-ray spectroscopy (WDXS), which was performed on the electron microprobe Cameca SX100 using Mg$_5$Sn and elemental Pt as standards for the intensity measurements of the Mg Kr and Pt L$_x$ X-ray lines at an acceleration voltage of 20 kV. Applying the ZAF matrix correction model led to analytical totals of 100.6(2) wt %. Powder XRD was performed with a Guinier-Huber Image Plate Camera G670, Cu K$_{α}$ radiation ($\lambda$ = 1.54056 Å) with LaB$_6$ as internal standard. Small crystals of the phase were selected from the crushed annealed samples. The splitters were glued to thin glass fibers and were analyzed at room temperature using a Rigaku AFC7 diffractometer equipped with a Saturn 72+ CCD detector (Mo K$_{α}$ radiation, $\lambda$ = 0.71073 Å). The lattice parameters from the refinement of the powder and single-crystal data are in good agreement. Absorption correction was performed by a multi-scan procedure. All crystallographic calculations were performed with the program package WinCSD.$^{31}$

The Dresden Grand ARM, a double-corrected JEM-ARM300F microscope, was used for aberration-corrected TEM and HAADF-STEM imaging at 300 kV.$^{32}$ The images were recorded on a 4k × 4k pixel CCD array (Gatan US4000).

The all-electron, full-potential local-orbital method (FPLO) within the local density approximation$^{33}$ and the Perdew–Wang parametrization$^{34}$ was employed for quantum chemical calculations on four ordered models described in the main text. Experimentally obtained lattice parameters and atomic coordinates were employed for the calculations. Due to the large size of the unit cell with ca. 400 atoms, the calculations were extremely expensive in computation time.

The analysis of the chemical bonding in position space was performed by means of the electron localizability approach. For this purpose, the electron localizability indicator (ELI) in its ELI-D representation$^{35,36}$ and the electron density (ED) were calculated with a specialized module in the FPLO code.$^{37}$ The topologies of ELI-D and ED were evaluated by means of the program DGrid.$^{38}$ The atomic charges from ED and bond populations for bonding basins from ELI-D were obtained by the integration of ED within the basins (space regions) bound by zero-flux surfaces in the corresponding gradient field. This procedure follows the quantum theory of atoms in molecules (QTAIM).$^{41}$

### 3. RESULTS AND DISCUSSION

The X-ray powder diffraction pattern of Mg$_{29−x}$Pt$_{4+y}$ synthesized from the elements (nominal sample composition, Mg$_5$Pt) was indexed on the basis of a face-centered cubic unit cell with $a$ = 20.1068(2) Å (Figure S1). The powder XRD pattern of the Mg-rich sample Mg$_5$Pt showed small amounts of elemental Mg as impurity; this was also observed in the metallographic analysis (Figure S2). The powder XRD pattern of the Mg-deficient sample Mg$_5$Pt showed reflections of the impurity Mg$_5$Pt. The slightly smaller lattice parameter $a$ = 20.1045(2) Å of the majority phase Mg$_{29−x}$Pt$_{4+y}$ indicates a possibly quite narrow homogeneity range of the latter. The compound is formed by the peritectic reaction at 576(2) °C from Mg$_5$Pt and Mg-rich melt (Figures S2 and S3).

The crystal structure was solved using 2487 symmetry independent reflections from single-crystal diffraction data in the non-centrosymmetric space group $I4/3m$ (Table 1). The positions of three symmetry-independent Pt and nine Mg atoms (Mg1–Mg7, Mg9, Mg10, cf. Table 2) were easily refined, revealing a high level of ordering in the structure. The large atomic displacement parameter for the Mg8 site indicated its chemically analogous but non-complex Be$_5$Pt.

The refinement of their occupancy factors reveals that at Mg11 (Mg11 is present) and Mg12 (Mg8 is not occupied). The independent refinement of their occupancy factors reveals that at Mg11 there is more ED and at Mg12 there is less ED than required by the expected occupancy ratio of 0.74:0.26. In the case of Mg11, this leads to a rather unusual partial occupancy by Pt. The final refinement resulted in occupancies of 58% Mg + 5% Pt for Mg11 and 15% Mg for Mg12. The refinement converged to a final $R$ value of 0.0262 (Table 1). A partial occupancy of the Mg8 and Mg12 sites by Mg and a mixed occupancy by Mg/Pt of the Mg11 site yielded refined compositions of 87.5 at. % Mg and 12.5 at. % Pt, in good agreement with the WDXS analysis, which shows 87.6(1) at. % Mg and 12.4(1) at. % Pt (Table S1 and Figure S2). The refined atomic coordinates together with the equivalent displacement parameters are listed in Table 2. The anisotropic atomic displacement parameters and the interatomic distances can be found in Tables S2 and S3, respectively. Another possibility to refine the structure is to consider the presence of a Pt atom in the 4a position (Figure S8, Tables S4–S6). As may be expected, in this case, the residual value $R$ does not change markedly; it even increases.
Table 1. Crystallographic Data for Mg$_{29-x}$Pt$_{4+y}$ ($x = 0.47$, $y = 0.07$)

| composition | Mg$_{54.83}$Pt$_{54}$ |
|-------------|---------------------|
| space group | F43m                |
| Pearson symbol | rF391.2              |
| formula units per unit cell, Z | 12                   |
| unit cell parameters, a | 20.1068(2) Å$^a$ |
| unit cell volume, V | 812.88(3) Å$^3$ |
| calculated density, ρ | 3.63 g cm$^{-3}$ |
| crystal shape | irregular             |
| crystal size | 0.080 × 0.090 × 0.095 mm$^3$ |
| diffraction system | RIGAKU AFC7 |
| detector | Saturn 724+ CCD |
| radiation, wavelength, λ | Mo Kα, 0.71073 Å |
| scan type; step per degree; N(images) | φ, 0.5, 1140 |
| 2θ$_{max}$ | 79.96° |
| measured range in hkl | $-35 \leq h \leq 36$ |
| absorption coefficient | multi-scan |
| absorption correction | 22.61 mm$^{-1}$ |
| T(max)/T(min) | 0.22/0.14 |
| N(hkl) measured | 41,127 |
| N(hkl) unique | 2487 |
| observation criteria | F(hkl) $\geq 4σ(F(hkl))$ |
| number of refined parameters | 65 |
| R$_{B}$, R$_{w}$ | 0.0262, 0.0273 |
| largest diff. peak and hole (e$^-$ Å$^{-3}$) | −0.11/0.13 |

Table 2. Atomic Coordinates and Isotrop Displacement Parameters for Mg$_{29-x}$Pt$_{4+y}$ ($x = 0.47$ and $y = 0.07$; Space Group F43m)

| atom | site | x/a | y/b | z/c | U$_{eq}$/1000 (Å$^2$) $^a$ |
|------|------|-----|-----|-----|--------------------------|
| Pt1  | 16e  | 0.58148(1) | x  | x  | 0.01292(4) |
| Pt2  | 16e  | 0.84958(1) | x  | x  | 0.01218(4) |
| Pt3  | 16e  | 0.34382(1) | x  | x  | 0.01207(4) |
| Mg1  | 16e  | 0.4480(2)  | x  | x  | 0.0156(4)  |
| Mg2  | 24g  | 0.6438(2)  | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.0139(6)  |
| Mg3  | 24f  | 0.317(2)   | 0  | 0  | 0.0195(8)  |
| Mg4  | 48h  | 0.0993(1)  | x  | 0.2283(2) | 0.0214(5)  |
| Mg5  | 48h  | 0.05124(9) | x  | 0.8398(2) | 0.0182(5)  |
| Mg6  | 24g  | 0.1327(2)  | $\frac{1}{4}$ | $\frac{1}{4}$ | 0.0175(7)  |
| Mg7  | 48h  | 0.1939(1)  | x  | 0.9814(2) | 0.0166(5)  |
| Mg8  | 4a   | 0       | 0  | 0  | 0.019(3)   |
| Mg9  | 48h  | 0.15489(9) | x  | 0.4771(1) | 0.0153(4)  |
| Mg10 | 48h  | 0.10690(8) | x  | 0.7154(1) | 0.0145(4)  |
| Mg11 | 16e  | 0.0834(1)  | x  | x  | 0.0164(5)  |
| Mg12 | 16e  | 0.063(1)  | x  | x  | 0.018(5)   |

$^a$U$_{eq}$ = 4/3[U$_{11}(a^*)^2$] + ... + 2U$_{23}(b^*)^2(c^*)^2$ | c$^*$ cos (α$^*$)] + U$_{iso}$ for Mg8 and Mg12.

The refined composition turns out to not change essentially (87.7 at. % Mg and 12.3 at. % Pt).

The observed SOFs are understood as superposition of four different local ordering variants around the origin (all other positions are the same in all four models):

Model 1: Mg8 and Mg11 occupied by Mg (unit cell composition, Mg$_{54.83}$Pt$_{54}$);
Model 2: Mg8 non-occupied, Mg12 occupied by Mg (Mg$_{54.83}$Pt$_{54}$);
Model 3: Mg8 occupied by Mg, Mg11—by Pt (Mg$_{33}$Pt$_{64}$); Model 4: Mg8 occupied by Pt, Mg11—by Mg (Mg$_{34}$Pt$_{62}$).
From the effective charges (cf. bonding analysis below), other models with simultaneous occupation of both sites by Pt or Pt at Mg11 and non-occupied Mg8 position are considered as less probable because of the local agglomeration of negative charged species. The results of bonding analysis are visualized using models all four models (QTAIM charges) or model 2 (ELI-D analysis).

The appearance of local atomic arrangements corresponding to the four models mentioned above was verified by atomic-resolution TEM. The experimental HAADF-STEM image shows predominantly the positions of Pt atoms (atomic columns, Figure 1, top). The regions which were not exposed for a long time to the electron beam (Figure 1, middle) revealed besides the “regular” Pt atoms Pt1, Pt2, and Pt3, additional Pt at the positions Mg11 (model 3, more often, green circles) and Mg8 (model 4, quite rare, light pink circles), as well as regions where Pt was absent at these positions (models 1 and 2, yellow circles).

The crystal structure of Mg$_{29-x}$Pt$_{4+y}$ is close to being isopointal to the well-known Samson’s Mg$_3$Pd$_{12.69}$ (Mg$_{58.35}$Pd$_{43}$) or Mg$_{58.35}$Pd$_{43}$). In the prototype palladium (Pd) compound, the Mg8 position shows defects, and the Mg11 position is commonly occupied by Mg and Pd; only the split position Mg12 was not found in the original publication. According to the group–subgroup relations, Mg$_{29-x}$Pt$_{4+y}$ is a face-centered 2 × 2 × 2 superstructure of primitive Pd$_3$Cd$_4$ (space group P43m, a = 9.9415 Å, Figure S4), which—in turn—can be derived from the γ-brass arrangement. Usually the γ-brass derivatives are described by means of the nested polyhedral approach$^{12-14}$ analyzing the nearest environment of the high-symmetry points. In the case of Mg$_{29-x}$Pt$_{4+y}$, these are the point symmetry complexes 43m at (000), (1/4, 1/4, 1/4), (1/2, 1/2, 1/2), and (1/4, 1/4, 1/4), as well as at translationally equivalent points (Figure 2). The first nested polyhedral unit centered at (000) is the so-called α-Mn-type unit.$^{12}$ In this arrangement, a central atom (C) is surrounded by a tetrahedron (T), the second shell is formed by a truncated tetrahedron of 12 atoms (TT), and, finally, a cuboctahedron (CO) of 12 atoms forms the outer shell for a total of 29 atoms in the unit. The T$_{Ni}$-type nested polyhedral unit$^{11}$ is centered at (1/4, 1/4, 1/4) and contains 34 atoms. The first shell is here an octahedron (OH), followed by an outer tetrahedron (OT) which is capping four of the eight triangular faces of the OH, the latter is inserted in a cuboctahedron CO (cantellated tetrahedron), and the final outermost shell is formed by a TT. Finally, a γ-brass nested polyhedral unit$^{11,42}$ is found at (1/2, 1/2, 1/2). Here, the first shell is an empty regular inner tetrahedron, followed by an OT, the latter is inserted in a regular octahedron (OH), and the final shell is a cuboctahedron (CO), which completes the γ-brass unit.

Starting with the nested polyhedral units at (1/4, 1/4, 1/4) and (1/4, 1/4, 1/4) and adding the following shells, the crystal structure of Mg$_{29-x}$Pt$_{4+y}$ can be interpreted as a framework of interpenetrating or face-sharing crystallographic Mackay clusters with Pt2 atoms forming the OT (Figures 3, S5, S9).$^{35}$ The voids left in the unit cell are filled by tetrahedral

slightly to 0.027, and the refined composition turns out to not change essentially (87.7 at. % Mg and 12.3 at. % Pt).

The observed SOFs are understood as superposition of four different local ordering variants around the origin (all other positions are the same in all four models):
units of four tricapped trigonal prisms PtMg\textsubscript{9} centered by Pt3 atoms and by Pearce clusters\textsuperscript{44} centered by OT(Pt1). The latter cluster can be described as being built of four fused icosahedra having centers at the vertices of the OT tetrahedron (Figure 3). The crystallographic cluster approach opens an easier way to visualize the complex crystal structure of Mg\textsubscript{29-}\textit{x}Pt\textsuperscript{4+}\textsubscript{y}. Such crystallographic constructions allow the visualization of crystal structures, but leave open the question about their chemical roots. Thus, for the understanding of the reasons of the observed structural complexity and its influence on the properties of this material, further studies of chemical bonding are shown to be helpful.

To start with, the band structure calculations for the four structural models indicated that the observed disorder does not crucially influence the electronic density of states (DOS) for Mg\textsubscript{29-}\textit{x}Pt\textsuperscript{4+}\textsubscript{y} (Figure S6). Being mainly defined by the Pt-d states, it shows one large region with a wide maximum between $-4$ and $-3$ eV (the regular Pt positions occupied only models...
1 and 2) or between −4 and −2 eV (Pt at Mg8 or Mg11 sites, models 3 and 4). Less dependent on model and composition, a shallow minimum with non-negligible DOS around the Fermi level is found to indicate metal-like behavior for all models. Similar DOS features were recently observed in Be$_3$Pt$_5^{28}$ and Be$_5$Pt$_3^{29}$ and interpreted as a result of complete filling of the valence electron band in a multi-center bond system combined with a strong charge transfer (cf. below).

Furthermore, Mg$_{29-}$Pt$_{15+}$ shows an average atomic volume of 20.8 Å$^3$ that is significantly smaller than the atomic volume of 22.2 Å$^3$ calculated for the experimental composition using the atomic volume of 23.25 Å$^3$ for Mg and of 15.15 Å$^3$ for Pt. Such a volume contraction indicates strong Mg–Pt interactions in the compound. In order to shed more light on the interplay between the described crystallographic features and the atomic interactions, further analysis of chemical bonding was performed employing quantum chemical techniques in the position space. Such an approach recently evolved to a powerful bonding-investigation tool, in particular for intermetallic compounds with a low electron number in the last shell per atom (<2) and multi-atomic bonding (e.g., refs 20–21, and 30 and references therein).

Effective charges were evaluated within the QTAIM. For this purpose, the atomic shapes were obtained by employing the zero-flux surfaces in the gradient vector field of the ED, which form the boundaries of ED basins (QTAIM atoms, Figure 4). The so-obtained shapes are similar to those described for the chemically homologous compounds Be$_3$Pt$_5^{28}$ Be$_5$Pt$_3^{29}$ and Mg$_5$GaIr$_5$. The Mg atoms reveal compact convex polyhedra, and Pt shows large units with concave faces. Integration of the ED within these atomic basins yields their electronic population; subtracting the atomic number from the latter results in the effective charge. The latter follow the difference in the electronegativity of the elements. While Mg atoms typically have charges between +0.7 and +1.3 (for comparison, +1.2 to +1.4 in Mg$_5$GaIr$_5$), Pt has a strong negative charge with −4.5 to −5.2 (cf. −4.8 to −5.7 in Be$_3$Pt$_5$ and −4.0 in Be$_5$Pt$_3$). Most interesting are the calculated charge values in the region around the origin. In the case of model 1 (Mg8 and Mg11 are occupied by Mg, first line for atomic charges in Figure 4, top), the charge of Mg8 is rather small with +0.5, the next neighboring Mg11 has an even negative charge, and its neighbor Mg7 also has a reduced positive charge of +0.2 only. All these indicate an unfavorable agglomeration of particles with positive charge in this region in the sense of second Pauling’s structural principle for ionic materials (local electroneutrality). Indeed, removing Mg8 (model 2, second line for atomic charges in Figure 4, top) already improves the situation: Mg12 (split of Mg11), Mg5, and Mg7 attain all small positive charges. The appearance of Pt at the Mg11 site (model 3, third line for atomic charges in Figure 4, top) indeed improves the situation: both Mg8 and Mg5 show clearly positive charges of +1.4 and +0.9, respectively; Mg7 remains slightly positive (+0.3). A similar effect has the occupation of the Mg8 position by Pt (model 4, fourth line for atomic charges in Figure 4, top): Mg11, Mg5, and Mg7 positions show positive charges. The results of effective charge calculations mentioned above allow us to understand the appearance of Pt atoms at the Mg11 and Mg8 positions indicated by the crystal structure refinements and TEM study.

Recent analysis of chemical bonding, employing the electron localizability approach, in the chemically related compound Be$_3$Pt$_5$ with a crystal structure of similar complexity showed that the nested polyhedral units mark places of the multiatomic bonding, for example, the ELI-D reveals maxima at the centers of nested polyhedral units in Be$_3$Pt$_5$: half of the γ-brass units reflect 8- and 10-atomic bonds and the second half of 4- and 5-atomic bonds. In contrast, the ELI-D distribution in the (110) plane in Mg$_{29-}$Pt$_{15+}$ (model 2, Figure 5) does not show maxima at the high-symmetry points with 43m point symmetry at (000), (1/4 1/4 1/4), (1/2 1/2 1/2), and (1/4 1/4 1/4). Evaluation of more than 1500 bonding attractors in the valence region in Mg$_{29-}$Pt$_{15+}$ (Figure S7) shows that the absolute ELI-D maxima in this plane are located in the vicinity of the origin (position (0 0 0); region 1 in
Figure 5. ELI-D distribution in the (1 1 0) plane of the Mg$_{29-x}$Pt$_{4+y}$ unit cell (model 2). Positions of the four nested polyhedron clusters shown by filled yellow circles do not reveal ELI-D attractors. Two regions with the maximal values of ELI-D in this plane are shown with empty yellow circles. The shortest Pt3–Mg distances (brown) are shown for orientation.

Figure 6. Organization of the chemical bonding in Mg$_{29-x}$Pt$_{4+y}$ (model 2). (Top left) Two types of homoatomic 6a-bonds (cf. regions 1 and 2 in Figure 5) involving only Mg atoms (light pink shapes); six items of the first kind form a large edge-bridged tetrahedron centered at (000); the second type of six atomic bonds yields a small arrangement formed by Mg only. (Bottom left) Six atomic bonds in the unit cell represented by isolated pink and yellow polyhedrons. (Top right) Atomic arrangements around the Pt atoms based on heteroatomic interactions: upper line—the Pt QTAIM shapes; middle line—the Pt atoms surrounded by the Mg ligands in the QTAIM representation; bottom line—the basins of multi-atomic bonds involving Pt atoms (filled shapes of different colors) located in most part within the QTAIM shapes of Pt atoms (transparent shapes). (Bottom right) Super-tetrahedrons formed by atomic arrangements around Pt atoms and centered at ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$), and ($\frac{3}{4}$, $\frac{3}{4}$, $\frac{3}{4}$) for Pt1, Pt2, and Pt3, respectively. (Middle panel) Interconnection of the Pt-based super-tetrahedrons by homoatomic 6a-bonds in the crystal structure of Mg$_{29-x}$Pt$_{4+y}$.
Pt3). The Pt2 and Pt3 units do not have common vertices, but both share vertices with the Pt1 unit (Figure 6, bottom right). The Pt1, Pt2, and Pt3 units are interconnected by the 6a-Mg2Mg6Mg7-Mg9 bonds, and additionally Pt2 and Pt3 units are interlinked by the 6a-Mg4Mg5Mg7 bonds (Figure 6, middle).

Such a local spatial separation of regions with different bonding types—homoatomic 6a-bonds and heteroatomic multicenter bonds with Pt participation—differs clearly from the bonding picture of the structurally and chemically similar compound Be2Pt5, where the multi- and hetero-atomic polar Be–Pt bonds are regularly distributed in the unit cell containing ca. 400 atoms. The most probable explanation is the larger electronegativity difference in the case of the title compound if compared with the Be–Pt phases. From this point of view, the bonding picture in Mg29–Pt4+y with spatially separated homo- and hetero-atomic interactions is rather new for the CMA compounds. One should note here that there are only few examples of the complete bonding analysis of the CMA compounds, which does not allow more general remarks. The expected appearance of further bonding patterns in the CMA family is a consequence of the systematic experimental research and discovery of its new representatives, for example, refs 46–48.

4. CONCLUSIONS

The compound Mg29–Pt4+y belongs to the family of complex intermetallic compounds (CMA). Its cubic crystal structure with ca. 400 atoms in the unit cell can be geometrically described in terms of interpenetrating and face-sharing different crystallographic cluster types originating from nested polyhedral units located at the high-symmetry points in the unit cell, leaving open the chemical reasons for such complexity. Quantum chemical analysis of bonding in Mg29–Pt4+y employing the position space approach reveals a strong contribution of charge transfer and two types of multi-atomic bonds to the stabilization of the complex crystal structure. Structure building units around the Pt atoms (Pt1, Pt2, and Pt3) are formed by means of heteroatomic 3a-, 4a-, and 5a-bonds. The group of homoatomic 6a-bonds involving only Mg atoms is found to agglomerate around the origin of the unit cell and interconnect all three Pt-based units. Another group of 6a-bonds interlinks Pt2 and Pt3 units. Spatial separation of regions with different bonding features makes the key difference between Mg29–Pt4+y and other CMAs—derivatives of the γ-brass atomic arrangement—characterized by a homogeneous distribution of predominantly polar multi-center heteroatomic bonds in the unit cell.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02653.

Description of experimental and calculational techniques, electronic DOS, and details of structure evaluation and bonding analysis (PDF)

Accession Codes

CCDC 2184841 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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