Abstract: A niccolite series of [bnH$_2$$^{2+}$][M(HCOO)$_3$]$_2$ (bnH$_2$$^{2+}$ = 1,4-butyldiammonium) shows four kinds of metal-dependent phase transitions, from high temperature/pressure-induced ferro- to antiferro-, glass-like, and para-electric phases. The conformational flexibility of bnH$_2$$^{2+}$ and the different size, mass, and bonding character of the metal ion lead to various disorder-order transitions of bnH$_2$$^{2+}$ in the lattice and relevant framework modulations, thus different phase transitions and dielectric responses. The magnetic members display a coexistence or combination of electric and magnetic orderings in the low-temperature region.

Metal-organic frameworks (MOFs), now belonging to a large class of condensed matter, have shown great varieties, potentials and impacts in solid-state chemistry and physics.[1] Their inorganic–organic hybrid characters[1-2] allow the occurrence of various phase transitions, critical phenomena, and related properties, which have recently aroused great interest.[3-7] Ammonium metal formate frameworks (AMFFs) along this line are attractive,[8-18] their reversible phase transitions, at the individual critical temperatures, have recently been started.[9-15] Here we report a niccolite AMFF series of [bnH$_2$$^{2+}$][M(HCOO)$_3$]$_2$ in which bnH$_2$$^{2+}$ is 1,4-butyldiammonium and M runs through divalent Mn, Fe, Co, Ni, Cu, Zn, and Mg. The compounds are named 1Mn, 2Fe, 3Co, 4Ni, 5Cu, 6Zn, and 7Mg (3Co and 7Mg were reported before,[10] and the phase-transition character of 3Co was unknown). To date, the major explored AMFFs involve various monoaamoniums, and for the series incorporating the same ammonium but different metal ions, such as [NH$_4$][M(HCOO)$_3$][10, 12b, 13, 14] and ([CH$_3$)$_2$NH] [M(HCOO)$_3$][10c, 15], the observed phase-transition types could not be beyond two. Incorporating di-, tri-, or polyammoniums in AMFFs has been started.[10, 12b, 16] The conformational flexibility of polyammoniums adds another dimension, that is, the increased number of possible ordered states will probably result in more kinds of disorder-order transitions of polyammonium thus more complicated and interesting phase-transition patterns.[15b] The seven compounds were prepared by using 1,4-butyldiammonium, HCOOH, and metal perchlorate in methanol (see the Experimental Section and Table S1, in the Supporting Information).[8] Their phase purity were confirmed by powder X-ray diffraction (Figure S1, Supporting Information), and their decompositions were in the sequence of 5Cu (385 K) < 6Zn < 2Fe (410 K) < 3Co < 1Mn < 4Ni (433-437 K) < 7Mg (470 K) (Table S2 and Figures S2a, S2b, Supporting Information). The DSC runs (Figures S2c, S2d, Supporting Information) revealed their reversible phase transitions, at the individual critical temperatures ($T_C$) of 345 (1Mn), 231 (2Fe), 246 (3Co)[16b], 257 (4Ni), 244 K (5Cu; two peaks indicated probably two phase transitions), 233 (6Zn), and 405 K (7Mg[12b]). The DSC peaks, and the values of $\Delta H$ by integration of DSC peaks, $\Delta S = \Delta H/T_C$ and $N$ (the ratio of the state numbers in different phases) by $\Delta S = k\ln(N)[19]$ were prominent for 1Mn, 5Cu, and 7Mg, less prominent for 3Co and 6Zn, and quite small for 2Fe and 4Ni. The oscillation images (OSCIs, Figure S3 to S5, Supporting Information) provided further information. On cooling, the HT single crystals of 1Mn, 5Cu, and 7Mg became twinned at LT. Therefore only lattice distortions occurred. For 3Co and 6Zn, many weak spots appeared in LT OSCIs among the bright spots of HT OSCIs. This indicated the happening of a large, 36-fold multiple unit cell, which is still scarce.[16c] Instead, for 2Fe
and 4Ni, the HT and LT OSCIs displayed no changes. Therefore, the phase transitions of 2Fe and 4Ni are probably glass-like.\textsuperscript{27a, 29} All above observations implied the different, metal-dependent characters of the phase transitions within the series.

The seven compounds are all niccolite type.\textsuperscript{12b, 16a, 17} The structures were determined at temperatures covering the phase transitions (Figure 1, and Tables S3, S4, and Figure S6 in the Supporting Information). At HT, the six members besides 5Cu are isostructural, in trigonal space group P31c. They possess binodal 3D metal-formate frameworks containing (4\textsuperscript{11}-6\textsuperscript{1}+) and (4\textsuperscript{4}-6\textsuperscript{6}) metal nodes in the ratio of 1:1, connected by anti-formates (Figure 1a), and the framework topology is (4\textsuperscript{11}-6\textsuperscript{1})(4\textsuperscript{4}-6\textsuperscript{6}). The bnH\textsubscript{2}\textsuperscript{2+} cation locates in the unique, elongated, trigonal symmetric framework cavity that is formed by two one-corner-missing cubanes twinned together (Figure 1b and Figure S6a, Supporting Information). The cation is trigonally disordered. The terminal NH\textsubscript{2}+ ends and the central ethylene part are in three orientations but the two side CH\textsubscript{3} groups locate on the 3 axis, which indicates the rotating or twisting motion of bnH\textsubscript{2}\textsuperscript{2+}. Each NH\textsubscript{2}+ site points towards one corner cube face of the cavity, forming several N–H–O H-bonds to the formate edges. Molecular geometries are as expected, and the interatomic distances and cell parameters show the decreased trend with the metal ionic radius.\textsuperscript{8, 9a, 16a, 18}

The six members besides 5Cu are classified in three groups according to their phase-transition behaviors. On cooling, 1Mn and 7Mg\textsuperscript{20} experienced a transition in which the lattice symmetry changed from the HT trigonal P31c to LT monoclinic Cc. The primitive unit cell of the LT C-centered lattice came from the slight distortion of the HT hexagonal unit cell, by the occurred difference in a and b, and the slight derivation from 120° in c. Below Tc, the motion of the two NH\textsubscript{2}+ ends of bnH\textsubscript{2}\textsuperscript{2+} first froze, but the central ethylene part became swing (Figure 1c). This alternation led to the loss of HT trigonal symmetry, and the twinning of the LT crystals. The swing motion of the central ethylene froze on further cooling, reaching the ordered state of bnH\textsubscript{2}\textsuperscript{2+} in the lattice at 100 K (Figure 1d). The cation has a zigzag middle (CH\textsubscript{3})\textsubscript{4} part, and the two terminal NH\textsubscript{2}+ ends above and below the (CH\textsubscript{3})\textsubscript{4} plane, showing N–C–C–C gauche conformations (assigned as trans-GG) with torsion angles of 68°. The transition is PE to FE, given the alternation in structural symmetry from HT nonpolar to LT polar, in Alzu notation 3m\textit{Fm\textsubscript{3}}\textsuperscript{11} and the estimated polarizations are 1.48 (1 Mn) and 1.51 μC cm\textsuperscript{-2} (7 Mg), according to the separation of the positive (NH\textsubscript{2}+ ends of bnH\textsubscript{2}\textsuperscript{2+}) and negative (anionic framework) charges at 100 K.\textsuperscript{12b} 3Co and 6Zn behaved very differently. After the transition, the lattice symmetry changed from HT P31c to LT R\textit{3c}, and the LT cell 36-fold multiplied the HT cell (Figure S4, Supporting Information). This is the second example of such a high-fold multiple unit cell observed to date, after \{[pnH\textsubscript{2}\textsuperscript{2+}(H\textsubscript{2}O))Mg(HCOO)\textsubscript{4}] (pnH\textsubscript{2}\textsuperscript{2+} is 1,3-propanedi-aminomonomium).\textsuperscript{16c} Such a change implied a PE to AFE transition, caused by the disorder-order alternations of bnH\textsubscript{2}\textsuperscript{2+} and the related framework distortion. Below Tc, the metal-formate framework has three unique neighboring cavities A, B, and C (Figure 1e). In 3Co, the bnH\textsubscript{2}\textsuperscript{2+} cations in A and B are ordered, and they all have the two terminal NH\textsubscript{2}+ ends on the same side of the plane of the zigzag middle (CH\textsubscript{3})\textsubscript{4} (assigned as cis-GG), with N–C–C–C torsion angles of 63–65°. In C, the disordered bnH\textsubscript{2}\textsuperscript{2+} is in three orientations, one major (occupancy 0.72) is cis-GG, and the two minor (occupancy 0.14 each) nearly extended. This disorder remained down to 105 K. For 6Zn, the situations of bnH\textsubscript{2}\textsuperscript{2+} in A and C are similar, but in B the cation showed two orientations at 180 K, which then froze to one orientation at 100 K. The LT molecular and H-bonding geometries show more diversity than HT ones, due to the structural distortion. For 2Fe and 4Ni, the LT structures are the same as HT ones. The phase transitions are probably PE to glass-like,\textsuperscript{20} and the bnH\textsubscript{2}\textsuperscript{2+} cations randomly froze in the lattice. At LT, large Mn\textsuperscript{2+} and light Mg\textsuperscript{2+} should allow the accommodation of larger, less compact trans-GG bnH\textsubscript{2}\textsuperscript{2+} of lower conformational energy in the frameworks, corresponding to

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The structures show: a) the topological view of the niccolite metal-formate framework, with one cavity highlighted in red; b) the cavity with threefold disordered bnH\textsubscript{2}\textsuperscript{2+} inside, representing the six HT phases except 5Cu; c) the partially disordered bnH\textsubscript{2}\textsuperscript{2+} at 290 K and d) the ordered bnH\textsubscript{2}\textsuperscript{2+} at 100 K in the cavity of 1Mn (see text); e) the three neighboring cavities in 3Co at 105 K showing the two ordered bnH\textsubscript{2}\textsuperscript{2+} in cavities A and B, and one three-fold disordered bnH\textsubscript{2}\textsuperscript{2+} in cavity C; the cavities in 5Cu at 290 K f) and at 100 K g) showing different disordered states of bnH\textsubscript{2}\textsuperscript{2+} (see text). Color scheme: violet blue spheres, metal nodes; violet blue bonds, formate; for bnH\textsubscript{2}\textsuperscript{2+}, black, C; cyan, N; white, H; all in space-filling mode.

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the PE–FE transitions with high $T_C$ but smaller and heavier Fe$^{2+}$, Co$^{2+}$, Ni$^{2+}$, and Zn$^{2+}$ can only accommodate the smaller and compact cis-GG bnh$_2$+ of higher conformational energy, thus PE–AFE/glass transitions with lower $T_C$. In other AMFF series, the Mn and Mg members usually have high $T_C$.[9,12b,13–15]

The minor difference in metal size could lead to different transition characters for 2Fe, 3Co, 4Ni, and 6Zn.

5Cu is special, as in other AMFF series.[9,14,15b,16a,18] The Jahn–Teller Cu$^{2+}$ ions are 4+2 elongated octahedral, so the framework is composed of zigzag Cu-formate chains by short basal Cu–O$_{HCOO}$ bonds further linked by the long axial Cu–O$_{HCOO}$ ones (Figure S6b, 6c, Supporting Information). The HT structure is very similar to the niccolite dmenCu ([dmenH$_2$+] [Cu(HCOO)$_2$]$_2$ and dmenH$_2$+ =CH$_3$NH$_2$(CH$_3$)$_2$NH.CH$_3$)$_2$[16d] both in space group $C2/C$. In dmenCu, the extending dmenH$_2$+ is completely ordered in the lattice. Instead, in 5Cu, the nearly extended bnh$_2$+ exhibits two very closed orientations (Figure 1f), which indicate limited swing movement of bnh$_2$+. After the transition, the LT phase became triclinic $P1$, in which the unit cell came from the distorted primitive cell of the HT $C$-lattice. At LT, bnh$_2$+ still exhibits two orientations; however, one CH$_3$NH$_2$ side was fixed, and the other side moved, with the NH$_3$ end flips in two positions, resulting in one cis-GG conformation (Figure 1g). The transition is PE to PE, according to the above transition characters.

The four-phase transition patterns within the present series are unusual, compared to the known AMFF series[9,12b,13–15] usually showing phase-transition patterns not beyond two. The subtle synergy of the conformational flexibility of bnh$_2$+ and the size, mass, and bonding character of the metal ion could lead to such various and interesting phase transitions.

The dielectric responses ($\varepsilon'$ and $\tan \delta$) of the materials strongly depend on the transition character and metal (Figure 2, see Figure S7 and Table S2, Supporting Information). The $\varepsilon'$ of 1Mn quickly dropped from approximately 40 at HT to less than 10 crossing $T_C$, and the $\tan \delta$ showed low values without relaxation. This is very different from 7Mg, a relaxor that displayed strong relaxation and great enhancement of $\varepsilon'$ for low frequencies (LF) below $T_C$.[16b] 1Mn and 7Mg experienced similar PE to FE transitions; however, the very different dielectric responses should be due to the larger and heavier Mn versus Mg, thus probably different lattice dynamics. 2Fe, 3Co,[16b] 4Ni, and 6Zn all feature strong dielectric dispersion. The HT $\varepsilon'$ values are approximately 30 for 2Fe, 3Co, and 4Ni, and 60 for 6Zn. The $\varepsilon'$-descending rate on cooling changed from slow of 2Fe to fast of 6Zn, and stepwise behavior of decreasing developed, more significant for LF. In LT, $\varepsilon'$ usually reached constant values of about 5. The $\tan \delta$ versus $T$ traces displayed a strong frequency ($\omega$) dispersion, and the $\tan \delta$ peaks corresponded to the fall in the $\varepsilon'$ traces due to the Kramers–Kronig relations.[20] The $\tan \delta$ peaks were smoothly from HT–HF (high frequencies) to LT–LF for 2Fe and 3Co, but stepwise behaviors around $T_C$ were clearly observed for 3Ni and 6Zn. The $f$ versus $T_p$ (the peak temperature in $\tan \delta$) data could be fitted by the Arrhenius law of $T_p = T_{0} \times \exp(E_{A}/k_{B}T)$ ($T = (2\pi f)^{-1}$,[22] resulting in the activation energy $E_{A}/k_{B}$ range of 5.5–6.3×10$^{-3}$ K or 0.47–0.54 eV, and the pre-exponential factors $T_{0}$: 1.3–7.6×10$^{-16}$ s (Figure S7h and Table S2, Supporting Information). For the four members, the rotate, twist, or flip motions of bnh$_2$+ at HT contribute high $\varepsilon'$ but low $\tan \delta$. On cooling the framework contraction and the increased H-bonding interactions slow or damp such motions then freeze into AFE or glassy states, resulting in the decrease/increase in $\varepsilon'/\tan \delta$ and the strong dielectric dispersion. The similar $E_{A}$ values are seemingly rational for the alternation of several N/C–H–O interactions required for the motions.[12b, 16b, 22] For 5Cu, the swing or flip motions of bnh$_2$+ at HT are more limited, or the amplitudes much smaller, compared to other members. Therefore, the $\varepsilon'$ values are two or more times smaller. The decrease of $\varepsilon'$ is quite slow, and for LF two-step descending is observed. This is because of the further limited motion of bnh$_2$+ with one CH$_3$NH$_2$ arm fixed in the LT PE phase, but another NH$_3$ end still flipped. The strong $f$-dispersion of $\tan \delta$ shows two well developed peak clusters in HT–HF and LT–LF regions, respectively, indicating different relaxation properties, corresponding to the different status of bnh$_2$+. However, the $f$ versus $T_p$ data could not be simulated by Arrhenius law.

The five magnetic members display typical magnetic behaviors (Figure 3, Figure S8 and Table S5, Supporting Information) of AMFFs.[19] Briefly, 1Mn, 2Fe, 3Co, and 4Ni show 3D AF ordering with weak ferromagnetism (WF) in the LT region, confirmed by the anomalies in dc susceptibilities, the zero-field-cooling and field-cooling (ZFC/FC) traces with quick rise and bifurcation behavior, the isothermal magnetizations with hysteresis, and the ac susceptibilities with peaks. The Neél temperatures are 9.1 K (1Mn), 19.8 K (2Fe), 9.9 K (3Co) and 28.2 K (4Ni), respectively, and 2Fe possesses large coercive field and sponta-
neous magnetization. For 5Cu, the Cu-formate framework consists of Cu–OCHO–Cu zigzag chains linked by the long axial Cu–O-formate bond. It thus exhibits low-dimensional magnetism. The χ versus T display a broad maximum around 43 K due to the strong intra-chain AF coupling. Then, the trace quickly further decreased down to 2 K, which indicated an inter-chain AF coupling or global AF ordering, which was further confirmed by the linear isothermal magnetization without hysteresis. Using the molecular field results, the magnetic couplings are estimated −0.43 K (1Mn), −1.0 K (2Fe), −4.0 K (3Co), and −8.7 K (4Ni). For 5Cu, the intra- and inter-chain couplings are estimated −44.5 and −4.6 cm−1, respectively, by simulating the HT susceptibilities with the Bonner–Fisher chain model.

In conclusion, a nicolette AMFF series was obtained by employing bnH4+, in which four different phase transitions were observed. The Mn and Mg members showed PE–FE transitions with lattice symmetry changed from HT non-polar P31c to LT polar Cc. The Co and Zn members underwent a PE–AFE phase transition from HT P31c to LT R3c with a rare 36-fold multiple unit cell. The Fe and Ni members experienced glassy transitions without alternation in the lattice symmetry. The Cu member displayed a PE–FE transition from HT C2/c to LT P1. The conformational flexibility of bnH4+ combined with the different characters (size, mass, and bonding) of metal ions lead to such various disorder-order transition patterns of bnH4+ and the relevant framework modulations, thus different phase-transition characters as well as dielectric responses. The basic structural–property relationships are established. However, many details, such as the FE/AFE/glass properties, thermodynamic and critical characters of the transitions, and so on, merit further extensive investigation. In LT, the magnetic members showed coexistence or combination of various electric and magnetic states, FE/AFE/dipolar glass/PE with WF/AF. They are of further interest for MOF-multiferroics. The present work demonstrates the wide variety in phase transitions and relevant properties of the AMFF class, which is becoming a good and valuable platform for relevant research.

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Keywords: diammonium metal formate · dielectricity · magnetism · metal–organic frameworks · phase transitions

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