Supporting Information

A solid-phase quasi-intramolecular redox reaction of [Ag(NH$_3$)$_2$]MnO$_4$ : an easy way to prepare pure AgMnO$_2$

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Figure S1. Powder X-ray diffractograms of products prepared by method of Klobb,[17] Scagliari and Marangoni [13] and in the reaction of Ag(NH$_3$)$_2$NO$_3$ and NaMnO$_4$. 
Figure S2. DSC Study on compound 1 between -150 and 25 °C
Figure S3. DSC Study on compound 1-ClO$_4$ between -150 and 25 °C
Figure S4. Powder XRD of orthorhombic HT-[Ag(NH$_3$)$_2$ClO$_4$] (compound 1-ClO$_4$).
Figure S5. Powder XRD of monoclinic HT-[Ag(NH$_3$)$_2$]$_2$MnO$_4$ (compound 1).
Figure S6. Powder XRD of solid solution contains ~ 28 and 72 mol % permanganate and perchlorate ions, respectively.
Figure S7. The packing of ions in the lattice of HT-1 compound.
Figure S8. The disordered ammonia molecule and its hydrogen bond system in compounds LT-1 and HT-1
Figure S9. The torsion angles of diamminosilver(1+) units in compounds LT-1 (a) and HT1 (b)
Figure S10. Temperature dependent IR spectra of compound LT-1
Figure S11. Temperature-dependent IR spectra of compound HT-1
Figure S12. Raman spectra (532 nm excitation) of compounds LT-1 and HT-1 at 123 and 183 K, respectively.
Figure S13. Far-IR spectrum of compound HT-1
Figure S14. Raman spectrum of decomposition products formed from compound HT-1 at 223 K during Raman measurement on irradiation with 532 nm laser light
Correlation analysis for polymorphs LT-1 and HT-1

The isolated permanganate ion has $T_d$ symmetry, and accordingly, four Raman and two IR ($F_2$ species) active modes can be expected: $\nu_1$ (symmetric stretching), $\nu_2$ (symmetric bending), $\nu_3$ (antisymmetric stretching) and $\nu_4$ (antisymmetric bending). The symmetric bending mode is doubly (E), whereas the $\nu_3$ and $\nu_4$ modes are triply ($F_2$) degenerate under the molecular symmetry ($T_d$). In principle, after removing the degeneracy levels completely, 9 internal modes of permanganate ion can be expected.

| Molecular group | Site group | Factor group |
|-----------------|------------|--------------|
| $T_d$           | $C_5$      | $C_{2h}$     |
| $\nu_1$        | $A_1$      | $A_g$ (\(\nu_1, \nu_2, 2\nu_3, 2\nu_4\)) |
| $\nu_2$        | $E$        | $B_g$ (\(\nu_2, \nu_3, \nu_4\)) |
| $\nu_3, \nu_4$ | $F_2$      | $A_u$ (\(\nu_2, \nu_3, \nu_4\)) |
|                 |            | $B_u (\nu_1, \nu_2, 2\nu_3, 2\nu_4)$ |

Figure S15. Correlation diagram for the internal modes of permanganate ion in compounds LT-1 and HT-1 (2 and 1 kind of permanganate ions, respectively)

The compound LT-1 has two different permanganate ion types, thus the number of vibrations is double than that for compound HT-1. The hindered rotations and translations of the permanganate anions are both triply degenerate, under $T_d$ symmetry. The total number of factor-group modes, due to the external MnO$_4^-$ vibrations (hindered translations and hindered rotations), is equivalent with $2 \times 12 = 24$ and 12 degrees of freedom for compounds LT-1 and HT-1, respectively.
The complex cation (Ag(NH₃)₂⁺) modes are decomposed into components of ammonia as ligand (C₃ᵥ) modes and to the translation of central silver ions. For the ammonia as a ligand, ν₁ is the symmetric stretching, ν₂ is the symmetric bending, ν₃ is the antisymmetric stretching and ν₄ is the antisymmetric bending modes. Both ν₃ and ν₄ are doubly degenerated (E) vibrations under C₃ᵥ. The total number of factor-group modes, due to the internal vibrations and 4 or 2 types of crystallographically different ammonia ligands, are 4 x 12 = 48 and 2 x 12 = 24 resulting in 48 and 24 vibrational degrees of freedom in compound LT-1 and HT-1, respectively.

The external modes (Tₓᵧ and Rₓᵧ) are doubly degenerate modes under C₃ᵥ. The total number of factor-group modes due to the external vibrations is doubled and quadrupled (a consequence of two and four crystallographic types of NH₃) and are equivalent with 4 x 12 = 48 and 2 x 12 = 24 vibration degrees of freedom for compounds LT-1 and HT-1, respectively.

Regarding the Ag⁺-ions, there are 3 modes of acoustic origin out of the total of 48 (compound LT-1) and 24 (compound HT-1) external modes, which belong to species A_u + 2B_u. 45 and 21 optical modes of translational origin, 72 and 36 optical modes of rotational origin and 84 and 42 optical modes due to internal vibrations for compounds LT-1 and HT-1, respectively.
Figure S17. Correlation diagram for permanganate ion external modes in compounds LT-1 and HT-1 (2 and 1 kind of permanganate ions, respectively)

Figure S18. Correlation diagram for ammonia external modes in compounds LT-1 and HT-1 (4 and 2 kind of ammonia, respectively)
Figure S19. Correlation diagram for silver(1+) external modes in compounds LT-1 and HT-1
UV spectroscopic results

The diffuse UV reflectance spectra of the solid solution of compound HT-1 (1 %) in HT-1-ClO$_4$ had a very broad band system, which might contain the orbital allowed ($^1A_1$-$^1T_2$)($t_{1g}$-2e) (480-580 nm) and ($^1A_1$-$^1T_2$)($t_{2g}$-t$_2$) (320-380 nm). The permanganate ($^1A_1$-$^1T_2$)(3$t_{2g}$-2e) transition is expected to be a weak band between 380 and 320 nm. The site symmetry of permanganate ion in compound HT-1-ClO$_4$ is C$_s$, thus $^1T_2$ level splits into three states of symmetry, A", A'(1) and A'(2), and this splitting can further complicate the band system. In the UV range below 260 cm$^{-1}$ the Ag 4d-5s transition and the N$_p$-Ag$_{5s}$ or O$_p$-Ag$_{5s}$ LMCT transitions could give signal.

Figure S20. Diffuse reflectance UV spectrum of compound HT-1
Figure S21. Thermal decomposition curves of compound HT-1 in argon and air atmosphere.
Figure S22. DSC of compound HT-1 in N₂ atmosphere
Figure S23. DSC of compound HT-1 in O2 atmosphere
Figure S24. XRD of the evaporation product obtained from the aq. extract formed in controlled temperature (under benzene) decomposition of compound HT-1.
Figure S25. IR spectra of as-synthesized NH4NO3. AgNO3 (purple), AgNO3 (blue), and the decomposition product of compound HT-1 at 125 °C (red).
Figure S26. XRD of the decomposition product of compound 1 HT after heating at 700 °C.
Figure S27. TG MS of compound 1 under air: 14 (N⁺) and 32 (O₂⁺), 30 (NO⁺) and 44 (N₂O⁺).
Figure S28. TG MS of compound 1 under argon: 14 (N⁺), 15 (NH⁺), 16 (NH₂⁺, O⁺), 17 (NH₃⁺, OH⁺), 18 (H₂O⁺), 28 (N₂⁺), 30 (NO⁺) and 44 (N₂O⁺).
Polymorphic crystal structures of diammine silver(I) permanganate measured at 100 K and 180 K.

Single crystal structures of two polymorphic modifications of [Ag(NH$_3$)$_2$]MnO$_4$ complex were determined at 100 K (LT-1) and 180 K (HT-1) respectively using MoK$_{\alpha}$ radiation. Both modifications crystallize in the monoclinic crystal system. The low temperature modification (LT-1) has the lower $P2/m$ symmetry, which is a maximal non-isomorphic symmetry subgroup of the space group of the high temperature modification (HT-1) which is $I2/m$. LT-1 is isomorphous to the known structure of [Ag(NH$_3$)$_2$]ClO$_4$ complex. The asymmetric unit of LT-1 contains four quarter silver(I) cations, four half ammonia ligands and two half permanganate anions. The contents of the asymmetric unit of HT-1 are one half of that of LT-1 due to its higher symmetry. The unit cells of the two modifications are quite similar (ESI Table 1 and ESI Figure 29).

![Figure S29.](image)

Comparison of the crystal packing of M-1 (a) and M-2 (b) (view from the direction of the b crystallographic axis)

The silver ions form infinite chains parallel to the $b$ crystallographic axis in both structures. The Ag-Ag distance is 3.010 Å for LT-1 and 3.034 Å for HT-1. The silver cations have two coordinated ammonia molecules and the ammonia hydrogens are disordered over two positions in both structures with 1:1 occupancy. Two permanganate anions are coordinated to the silver in both structures giving rise to an octahedral coordination around the silver ion (Figure S30) and to a three-dimensional coordination network. The atomic planes of nitrogen and oxygen atoms are perpendicular to the silver chain in all cases. The N-Ag-O angles are listed in ESI Table 2. In the HT-1 structure, the Ag-N bonds are lying on the $a$ and $c$ unit cell axes while in LT-1, the Ag-N bonds are tilted from the unit cell axis directions.

The Ag-Ag chains coincide with the two-fold rotation axes, the Ag-N bonds are lying on mirror planes and the Ag ions sit on inversion centres in both structures. All of the permanganate anions are cut in half by mirror planes. In the high temperature modification parallel to the 2-fold rotation axes, 2-fold screw axes appear, which connects the Ag-Ag chains to each other.

Besides, between every two mirror planes, a glide plane appears which
connects the Ag coordination sphere to each other. Thus, the permanganate anions are related by inversion centres.

**Figure S30.** Octahedral coordination of the silver cations

The Ag-N and Ag-O distances are listed in ESI Table 2-4 for both polymorphs. All of the permanganate oxygens are involved in hydrogen bonds with the ammonia hydrogens. Hydrogen bonds for **LT-1** and **HT-1** are listed in ESI Table 3. In the solid phase of \([\text{Ag(NH}_3\text{)}_2]\text{MnO}_4\), an extensive hydrogen bonded network is formed with the participation of the ammonia molecules and the permanganate oxygens. The ammonia hydrogens are disordered over two positions, which are in fact two different hydrogen bonding positions with the permanganate anions (Scheme-white and light blue hydrogens). A certain flexibility of the ammonia positions may be deduced on the basis of the two different hydrogen positions, i.e., the ammonia position can be switched between the two hydrogen bonding sites.

Calculated powder diffraction patterns for of the two polymorphs are compared on Figure S31.
Figure S31. Generated powder diffraction patterns of M-1 (a) and M-2 (b) (CuK$_\alpha$ radiation)
**Table S1.** Crystal data and structure refinement for compounds LT-1 and HT-1

| Property                              | LT-1                              | HT-1                              |
|---------------------------------------|------------------------------------|------------------------------------|
| Empirical formula                     | Ag1 H6 Mn1 N2 O4                   | Ag1 H6 Mn1 N2 O4                   |
| Formula weight                        | 260.865                            | 260.865                            |
| Temperature                           | 100.0(1)                           | 180.0(1)                           |
| Radiation and wavelength              | Mo-Kα, λ=0.71073 Å                 | Mo-Kα, λ=0.71073 Å                 |
| Crystal system                        | monoclinic                         | monoclinic                         |
| Space group                           | P 2/m                              | I 2/m                              |
| Unit cell dimensions                  |                                   |                                   |
| a=7.9095(5) Å                        | a=7.8112(3) Å                      |                                   |
| b=6.0205(4) Å                        | b=6.0682(2) Å                      |                                   |
| c=12.6904(11) Å                      | c=13.1260(5) Å                     |                                   |
| α=90°                                 | α=90°                              |                                   |
| β=98.056(7)°                         | β=96.438(4)°                       |                                   |
| γ=90°                                 | γ=90°                              |                                   |
| Volume                                | 598.34(8) Å                        | 618.25(4) Å                       |
| Z                                      | 4                                  | 8                                  |
| Density (calculated)                  | 2.896 Mg/m³                        | 2.803 Mg/m³                       |
| Absorption coefficient, μ             | 5.317 mm⁻¹                         | 5.145 mm⁻¹                         |
| F(000)                                | 496                                | 496                                |
| Crystal colour                        | colorless                          | colorless                          |
| Crystal description                   | prism                              | prism                              |
| Crystal size                          | 0.200 x 0.150 x 0.150 mm           | 0.50 x 0.20 x 0.15 mm              |
| Absorption correction                 | Multi-scan                         | Multi-scan                         |
| Max. and min. transmission            | 0.69743,1.00000                    | 0.61697,1.00000                    |
| θ–range for data collection           | 3.243 ≤ θ ≤ 29.862°                | 2.899 ≤ θ ≤ 29.881°                |
| Index ranges                          | -11 ≤ h ≤ 10; -8 ≤ k ≤ 8; -17 ≤ l ≤ 17 | -10 ≤ h ≤ 10; -8 ≤ k ≤ 8; -16 ≤ l ≤ 18 |
| Reflections collected                 | 1673                               | 6973                               |
| Completeness to 20 θ                  | 0.997                              | 1.000                              |
| Independent reflections               | 1673 [R(int) =0.0466]              | 921 [R(int) =0.0279]               |
| Reflections I>2σ(I)                   | 1279                               | 845                                |
| Refinement method                     | full-matrix least-squares on F2    | full-matrix least-squares on F2    |
| Parameters                                                                 | Value 1 | Value 2 |
|---------------------------------------------------------------------------|---------|---------|
| Data / restraints / parameters                                            | 1673 / 0 / 100 | 921 / 0 / 50 |
| Goodness-of-fit on $F_2$                                                 | 1.094   | 1.018   |
| Final $R$ indices [$I>2\sigma(I)$]                                       | $R_1 = 0.0356$, $wR_2 = 0.0807$, $R_1 = 0.0205$, $wR_2 = 0.0504$ |
| $R$ indices (all data)                                                   | $R_1 = 0.0519$, $wR_2 = 0.0886$, $R_1 = 0.0241$, $wR_2 = 0.0523$ |
| Max. and mean shift/esd                                                  | 0.000; 0.000 | 0.000; 0.000 |
| Largest diff. peak and hole                                              | 1.880; -0.978 e Å$^{-3}$ | 1.541; -0.639 e Å$^{-3}$ |
**Table S2.** Interatomic distances and angles in compounds **LT-1** and **HT-1**.

|        | LT-1                      |        |        |        |        |
|--------|---------------------------|--------|--------|--------|--------|
|        | **Ag1-N1**                | **Ag1-O4** | **2.69(2) Å** | **N1-Ag1-O4** | **89.4(8)**° |
|        | **Ag2-N2**                | **Ag2-O2** | **2.77(2) Å** | **N2-Ag2-O2** | **73.5(8)**° |
|        | **Ag3-N3**                | **Ag3-O5** | **3.04(2) Å** | **N3-Ag3-O5** | **85.9(8)**° |
|        | **Ag4-N4**                | **Ag4-O3** | **2.86(2) Å** | **N4-Ag4-O3** | **70.8(8)**° |

|        | HT-1                      |        |        |        |        |
|--------|---------------------------|--------|--------|--------|--------|
|        | **Ag1-N1**                | **Ag1-O2** | **2.685(2) Å** | **N1-Ag1-O2** | **81.2(1)**° |
|        | **Ag2-N2**                | **Ag2-O1** | **3.054(2) Å** | **N2-Ag2-O1** | **78.6(1)**° |
### Table S3. Comparison of Ag-Ag and Ag-N bond distances (Å) or NAgN angles (°) in [Ag(NH$_3$)$_2$]X compounds

| X(-)   | Temperature, K | $d_{\text{Ag-Ag}}$ | $d_{\text{Ag-N}}$ | N-Ag-N angles | Ref.               |
|--------|----------------|---------------------|-------------------|---------------|--------------------|
| MnO$_4$, LT   | 100            | 3.010               | 2.100; 2.115; 2.142; 2.150 | 180          | our work          |
| MnO$_4$, HT    | 180            | 3.034               | 2.112; 2.113      | 180          | our work          |
| ClO$_4$, LT    | 170            | 3.020               | 2.115; 2.139      | 180          | Nockemann, ZAAC   |
| ClO$_4$, HT    | 293            | 3.089               | 2.129; 2.138; 2.145; 2.160 | 180          |                   |
| SO$_4$, LT     | 298            | 3.200               | 2.110             | 174.3        | Zachw. Z. krist.  |
| NO$_3$          | 223            | 3.131               | 2.122; 2.125      | 180          | Yamaguchi, Acta Chem: Scand. |
| LT-1 |  |
|---|---|---|---|---|---|---|
| Donor --- H....Acceptor | D - H | H...A | D...A | D - H...A | symm. op. |
| N1 --H1A ..O1 | 0.89 | 2.57 | 3.24(2) | 132 | x,y,z |
| N1 --H1A ..O5 | 0.89 | 2.46 | 3.18(3) | 139 | 1-x,y,1-z |
| N1 --H1B ..O6 | 0.89 | 2.39 | 3.28(3) | 172 | -x,-2+y,1-z |
| N1 --H1C ..O2 | 0.89 | 2.20 | 3.074(6) | 169 | x,1+y,z |
| N2 --H2A ..O2 | 0.89 | 2.54 | 2.98(3) | 112 | x,y,z |
| N2 --H2A ..O6 | 0.89 | 2.31 | 3.16(2) | 162 | -x,-1+y,1-z |
| N2 --H2B ..O2 | 0.89 | 2.53 | 3.119(8) | 124 | x,-1+y,z |
| N2 --H2C ..O4 | 0.89 | 2.26 | 3.119(8) | 162 | x,y,z |
| N3 --H3A ..O1 | 0.89 | 2.60 | 2.98(2) | 107 | -1+x,y,-1+z |
| N3 --H3A ..O1 | 0.89 | 2.14 | 2.98(2) | 158 | -1+x,2-y,-1+z |
| N3 --H3B ..O3 | 0.89 | 2.53 | 3.148(9) | 127 | -x,1+y,1-z |
| N3 --H3C ..O3 | 0.89 | 2.27 | 3.148(9) | 169 | -x,y,1-z |
| N4 --H4A ..O5 | 0.89 | 2.47 | 3.152(8) | 134 | x,y,z |
| N4 --H4A ..O1 | 0.89 | 2.40 | 3.112(2) | 137 | 1-x,y,1-z |
| N4 --H4B ..O5 | 0.89 | 2.32 | 3.152(8) | 156 | x,-1+y,z |
| N4 --H4B ..O1 | 0.89 | 2.58 | 3.112(2) | 119 | 1-x,1-y,1-z |
| N4 --H4C ..O6 | 0.89 | 2.55 | 3.112(2) | 121 | x,-1+y,z |
| N4 --H4C ..O3 | 0.89 | 2.38 | 2.94(3) | 121 | -x,y,1-z |
| N4 --H4C ..O6 | 0.89 | 2.38 | 3.112(2) | 139 | x,2-y,z |
| HT-1 |  |
| Donor --- H....Acceptor | D - H | H...A | D...A | D - H...A | symm. op. |
| N1 --H1B ..O1 | 0.89 | 2.48 | 3.2903(1) | 152 | 3/2-x,1/2+y,3/2-z |
| N1 --H1B ..O3 | 0.89 | 2.41 | 3.0680(1) | 131 | 3/2-x,1/2+y,3/2-z |
| N1 --H1C ..O3 | 0.89 | 2.39 | 3.2487(1) | 162 | x,y,z |
| N1 --H1C ..O3 | 0.89 | 2.55 | 3.0680(1) | 118 | 3/2-x,3/2-y,3/2-z |
| N2 --H2A ..O3 | 0.89 | 2.15 | 3.0266(1) | 170 | x,1-y,z |
| N2 --H2B ..O3 | 0.89 | 2.51 | 3.0266(1) | 118 | x,-1+y,z |
| N2 --H2B ..O2 | 0.89 | 2.34 | 3.1651(1) | 154 | 1-x,-1+y,1-z |
Grinberg determined a parameter for ammine complexes based on the values of $\delta_s$(NH$_3$) between the uncoordinated (gaseous) ammonia (968 cm$^{-1}$) with RBS=0 and the most stable ammine complex ([Pt(NH$_3$)$_4$]Cl$_2$) (1370 cm$^{-1}$) with RBS=100. The RBS$_0$ is defined as the lowest experimental found RBS among the diamminesilver complexes which is supposed to the value without contribution of the hydrogen bond interaction (RBS$_0$=53.0).

**Table S5.** RBS values for [Ag(NH$_3$)$_2$]$^+$ cations in compounds LT-1 and HT-1 at various temperatures

| T, K (Compound) | RBS   | RBS-RBS$_0$ | H-bond contribution |
|----------------|-------|-------------|---------------------|
| 87 K, LT-1     | 66.9  | 13.8        | 20.6                |
|                | 64.5  | 11.4        | 17.8                |
|                | 57.6  | 4.5         | 7.8                 |
|                | 56.2  | 3.1         | 5.7                 |
|                | 54.8  | 1.7         | 3.3                 |
|                | 53.1  | 0.1         | 0.2                 |
| 180 K, HT-1    | 65.5  | 12.5        | 19.1                |
|                | 56.9  | 3.9         | 6.9                 |
|                | 55.2  | 2.2         | 4.0                 |
|                | 53.1  | 0.1         | 0.2                 |
| 300 K, HT-1    | 64.8  | 11.8        | 18.2                |
|                | 55.5  | 2.5         | 4.5                 |