Guido J. Reiss* and Marie Barbara Wolke

Hydrogen bonding in the crystal structure of nicotin-1,1′-dium tetrabromidomanganate(II)

https://doi.org/10.1515/ncrs-2025-0247
Received May 25, 2025; accepted July 16, 2025;
published online July 25, 2025

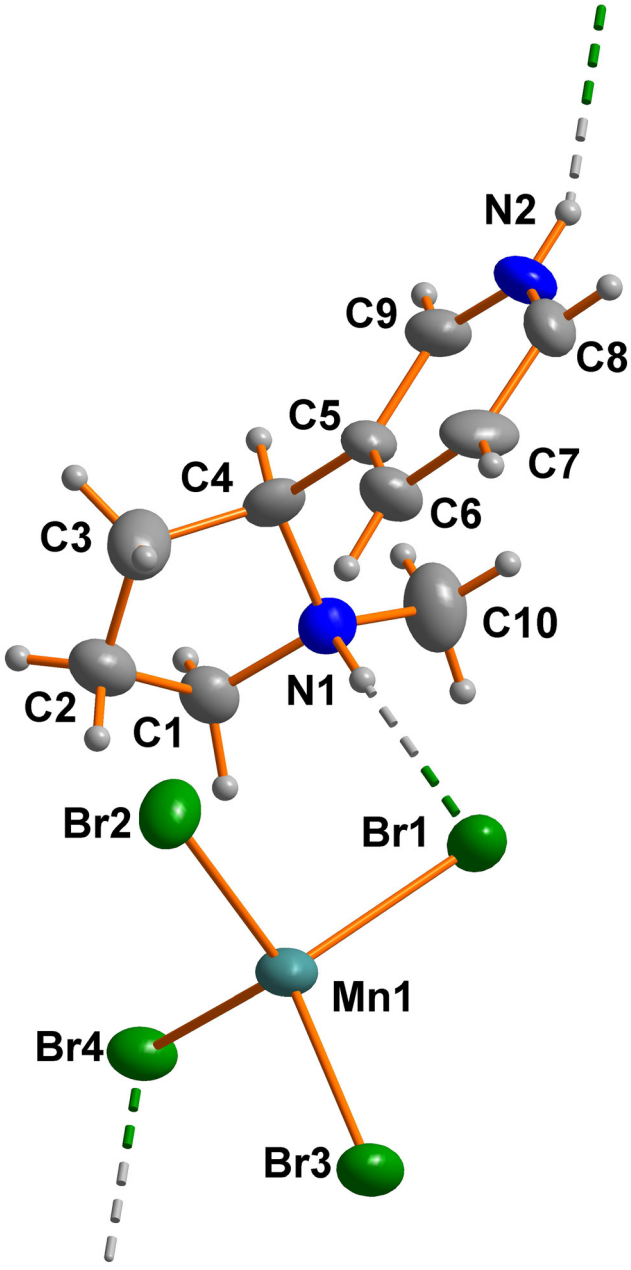
Abstract

$C_{10}H_{16}Br_4MnN_2$ monoclinic, $P2_1$ (no. 4), a = 7.4144(4) Å, b = 13.7490(8) Å, c = 8.3011(5) Å, β = 96.209(4)°, Z = 2, V = 841.26(8) Å^3, $R_{gt}(F)$ = 0.0458, wR_{ref} = 0.1245, Flack–Parsons-parameter: −0.02(2) [6], T = 293(2) K.

CCDC no.: 2473148

A selected region of the hydrogen bonded chained title crystal structure is shown in the figure.

Table 1 containing crystallographic data and the list of the atoms including atomic coordinates and displacement parameters can be found in the cif-file attached to this article.



1 Source of material

All reagents were obtained from commercial suppliers and used without further purification. The title compound was synthesized by dissolving nicotine in an aqueous solution of manganese(II) bromide prepared using concentrated hydrobromic acid (48 % HBr). The mixture was briefly heated to ensure complete dissolution of the nicotine. Upon standing at ambient temperature, orange block crystals of the title compound nicotin-1,1-dium tetrachloridomanganate(II) (systematic name: 3-((1*R*,2*S*)-1-methylpyrrolidin-1-ium-2-yl) pyridin-1-ium) tetrachloridomanganate(II) formed over the course of several days.

2 Experimental details

A crystal of the title compound was directly selected from the mother liquor and transferred to an IPDS-2T two-circle diffractometer.[1] An absorption correction (Multi–Scan method) was applied.[1]

The structure solution and the refinement were successfully carried out using the SHELX program system.[3–5]

All hydrogen atoms were seen in the difference electron density map after all non-hydrogen atoms were located. The figure was created using the Diamond software.[6]

***Corresponding author: Guido J. Reiss**, Bioanorganische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany, E-mail: reissg@hhu.de. https://orcid.org/0000-0002-3004-3955

Marie Barbara Wolke, Bioanorganische Chemie, Heinrich-Heine-Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany

Table 1: Data collection and handling.

Crystal:	yellow-orange blocks
Size:	0.20 × 0.25 × 0.30 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	10.3 mm^{-1}
Diffractometer, scan mode:	STOE IPDS-2T, φ and ω scans
θ_{max}, completeness:	27.5°, 99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8179, 3843, 0.093
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3,482
$N(param)_{refined}$:	162
Programs:	STOE,[1] SHELX,[2,3] ShelXle,[4] Diamond[5]

3 Introduction

A recent survey of the Cambridge Structural Database (CSD)[7] identified over 2 crystal structures containing doubly protonated nicotine. As previously reported and summarized by one of the authors,[8] structural data are also available for (a) metal complexes incorporating neutral nicotine ligands (b) a small number of co-crystals where nicotine is present as a neutral component (c) several pyrrolidinyl-monoprotonated nicotinium salts and (d) mono-protonated nicotinium acting as a cationic ligand. A recent report discusses the stabilization of $[Pb_3I_{11}]^{5-}$-clusters and $[PbI_3]^{-}$-polymers by protonated nicotinium cations.[9] This work is part of our ongoing research into the synthesis, structural characterization, and hydrogen-bonding patterns in salts derived from natural products such as nicotine,[10,11] as well as other commonly used everyday drugs.[13,14]

4 Molecular structure description

The asymmetric unit of the reported structure contains one nicotin-1,1′-dium dication (3-((1*R*,2*S*)-1-methylpyrrolidin-1-ium-2-yl)pyridin-1-ium, abbreviated as $nicH^{2+}$) and one tetrabromidomanganate(II) dianion (see the figure). As discussed in previous studies, [8,10–12]protonation at the nitrogen atom of the pyrrolidinyl ring introduces a second chiral center at N1 (see the figure), which consistently adopts the *R* configuration in all reliable entries in the Cambridge Structural Database.[7] The four carbon atoms of the pyrrolidinyl ring (C1–C4) of the $nicH^{2+}$ dication are nearly planar, with a root-mean-square deviation (RMSD) of 0.021 Å, while the N1 atom is displaced by 0.56(2) Å from this plane. The defined plane formed by C1–C4 shows an angle of 66.0(6)° with the mean plane of the pyridinylium moiety (see the figure). The bond lengths and angles within the $nicH^{2+}$ dication[8,10,11] as well as in the $[MnBr_4]^{2-}$ anion[15,16] are within the expected ranges. In detail the Mn–Br bond lengths in the complex are consistent, ranging from 2.498(2) Å to 2.514(2) Å.

5 Supramolecular aspects

The $nicH^{2+}$ dication participates in two N–H···Br hydrogen bonds that connects the cation to two neighboring $[MnBr_4]^{2-}$ anions [N1···Br1 = 3.241(11) Å N2…Br4# = 3.368(11) Å(# = *x*-1, *y*, *z*+1)]. By this connection a hydrogen bonded chain along [10–1] is created (see the figure).

Acknowledgements: We thank Eleonore Hammes for the data collection using the STOE–IPDS2T diffractometer.
Conflict of interest: The authors declare no conflicts of interest regarding this article.
Author contribution: Both authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

References

1. STOE et Cie., *X–Area–Software*: Darmstadt, 2012.
2. Sheldrick, G. M. A Short History of *SHELX*. *Acta Crystallogr.* **2008**, *A64*, 112–122.
3. Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr.* **2015**, *C71*, 3–8.
4. Hübschle, C. B.; Sheldrick, G. M.; Dittrich, B. ShelXle: A Qt Graphical User Interface for SHELXL. *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.
5. Brandenburg, K. DIAMOND. *Visual Crystal Structure Information System. Ver. 4.5.2*; Crystal Impact: Bonn, Germany, 2018.
6. Parsons, S.; Flack, H. D.; Wagner, T. Use of Intensity Quotients and Differences in Absolute Structure Refinement. *Acta Crystallogr*. **2013**, *B69*, 249–259.
7. Groom, C. R.; Allen, F. H. The Cambridge Structural Database in Retrospect and Prospect. *Angew. Chem. Int. Ed.* **2014**, *53*, 662–671.
8. Reiss, G. J. The Crystal Structure of 3-((1*R*,2*S*)-1-Methylpyrrolidin-1-ium-2-yl)pyridin-1-ium tetrachloridomanganate(II), $C_{10}H_{16}C_{l4}MnN_2$. *Z. Kristallogr. – N. Cryst. Struct.* **2020**, *235*, 415–417.
9. Fletcher, J. D.; Nag, J.; Yazdaanpanah, R.; Sarker, S.; Kulkarni, S.; Gilley, I. W.; Aydin, K.; Gopalan, V.; Kanatzidis, M. G. Mixed 1D/0D Structures of Chiral Hybrid Lead Halides with an l–Nicotinium Spacer Exhibit Broadband Photoluminescence and Polarized Emission. *J. Am. Chem. Soc.* **2025**, *147*, 8820–8831.
10. Reiss, G. J.; Sergeeva, A. The Crystal Structure of 3-((1*R*,2*S*)-1-Methylpyrrolidin-1-ium-2-yl)pyridin-1-ium tetrachloridocobaltate(II) Monohydrate, $C_{10}H_{18}Cl_4CoN_2O$. *Z. Kristallogr. – N. Cryst. Struct.* **2017**, *232*, 159–161.
11. Reiss, G. J. I_5-Polymers with a Layered Arrangement: Synthesis, Spectroscopy and Structure of a New Polyiodide Salt in the Nicotine/HI/I_2 System. *Z. Naturforsch.* **2015**, *B70*, 735–739.
12. Reiss, G. J.; Wyshusek, M.; Rheinländer, J. C.; Konovalova, I. S. Hydrogen Bonding and π-Halogen Interactions in the Crystal Structure of Bis(Theophyllinium) Hexachloridoplatinate(IV) Monohydrate. *Z. Kristallogr. – N. Cryst. Struct.* **2024**, *239*, 813–816.
13. Konovalova, I. S.; Shishkina, S. V.; Wyshusek, M.; Patzer, M.; Reiss, G. J. Supramolecular Architecture of Theophylline Polymorphs, Monohydrate and Co-crystals with Iodine: Study from the Energetic Viewpoint. *RSC Adv*. **2024**, *14*, 29774–29788.

14. Reiss, G. J. A Cyclic I_{10}^{2-} Anion in the Layered Crystal Structure of Theophyllinium Pentaiodide, $C_7H_9I_5N_4O_2$. *Z. Kristallogr. – N. Cryst. Struct.* **2019**, *234*, 737–739.
15. Rok, M.; Zarychta, B.; Janicki, R.; Witwicki, M.; Bieńko, A.; Bator, G. Dielectric–Optical Switches: Photoluminescent, EPR, and Magnetic Studies on Organic–Inorganic Hybrid (Azetidinium)$_2$ $MnBr_4$. *Inorg. Chem.* **2022**, *61*, 5626–5636.
16. Mao, L.; Guo, P.; Wang, S.; Cheetham, A. K.; Seshadri, R. Design Principles for Enhancing Photoluminescence Quantum Yield in Hybrid Manganese Bromides. *J. Am. Chem. Soc.* **2020**, *142*, 13582–13589.