Mendeleev Communications

Mendeleev Commun., 2025, **35**, 42–44

Synthesis and luminescent properties of a new manganese complex based on *N*-substituted bis(diphenylphosphoryl)pyrrolidine

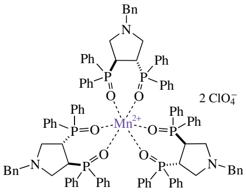
Eleonora E. Kim,[a] Dmitry S. Ionov,[b] Alexander D. Volodin,[a] Alexander A. Korlyukov,[a,c] Yuriy N. Kononevich[a] and Valery K. Brel*[a]

[a] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 119334 Moscow, Russian Federation. E-mail: v_brel@mail.ru*
[b] *Photochemistry Center, Kurchatov Complex of Crystallography and Photonics, National Research Center 'Kurchatov Institute', 119421 Moscow, Russian Federation*
[c] *N. I. Pirogov Russian National Research Medical University, 117997 Moscow, Russian Federation*

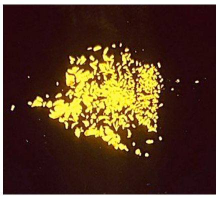
DOI: 10.71267/mencom.7577

A new luminescent Mn^{II} complex based on 1-benzyl-3,4-bis(diphenylphosphoryl)pyrrolidine ligand has been synthesized and fully characterized. This complex exhibits intense luminescence in the solid state (λ_{em} = 585 nm) with a high quantum yield (60%) as well as luminescence lifetime of 17 ms.

Daylight



QY = 60%



UV irradiation

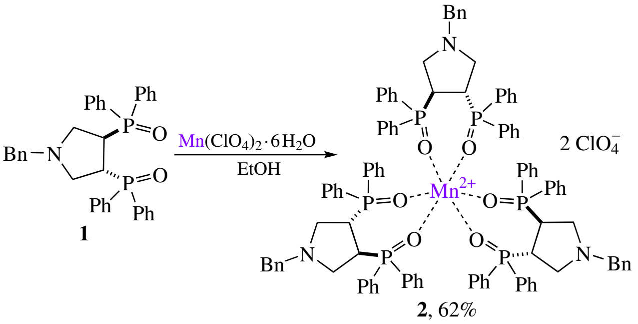
Keywords: luminescence, X-ray diffraction analysis, manganese(II) complexes, phosphorus-containing ligands, NMR spectroscopy.

Currently, organic and hybrid organo-inorganic manganese(II) complexes have attracted much attention due to their tunable optoelectronic properties, high stability and low toxicity.[1–3] The simple synthetic methods and unique photophysical properties of these complexes make them attractive candidates for the development of information storage and protection devices,[4] low-cost organic light-emitting diodes,[5–7] X-ray scintillators[8,9] and luminescent switches.[10,11] The luminescence of these complexes is caused by spin-forbidden d–d transitions of the Mn^{II} ion, which has a phosphorescent character and covers the spectral range from about 500 nm to the near-IR range.[1,3] Most of the manganese complexes reported in the literature were synthesized using nitrogen[10,12] and/or phosphorus[5,13–15] containing organic ligands.[4,16–20] For example, the organo-inorganic hybrid Mn^{II} complexes, [Mn(L)$_3$]MnHal$_4$, which exhibit bright dual-emission phosphorescence, were synthesized by reacting Mn^{II} halides with bis(phosphine oxide) ligands. These compounds combine tetrahedral and octahedral complexes in one structure, providing dual-emission behavior due to the luminescence of both species.[21] Complexes based on the triphenylphosphine oxide ligand can be used in luminescent printing of protected information.[13] Bright green triboluminescence in the potential hybrid ferroelectric compound (Ph$_3$PO)$_2$MnBr$_2$ was also documented.[22] Among individual complexes, coordination polymers can be obtained by treatment manganese ions with ligands possessing two or more coordination groups.[17,23] Thus, the study of new manganese complexes based on nitrogen- and phosphorus-containing ligands possessing valuable photophysical properties is a relevant direction.

In our previous study,[24] we described a new and efficient synthetic approach to the preparation of *trans*-bis-3,4-(diphenylphosphoryl)pyrrolidine (Pyrphos) ligand and its derivatives. In this work, we report the synthesis of manganese complexes based on bis(diphenylphosphoryl)pyrrolidines containing aromatic or aliphatic substituents. The synthesized compounds were characterized by physicochemical analysis methods, and the structure was determined by X-ray structural analysis. The optical properties were investigated by steady-state and time-resolved luminescence spectroscopy.

trans-1-Benzyl-3,4-bis(diphenylphosphoryl)pyrrolidine **1** used as a ligand to prepare manganese complex **2** (Scheme 1) was synthesized from 2,3-bis(diphenylphosphoryl)buta-1,3-diene and benzylamine (see Online Supplementary Materials, Scheme S1) by a method similar to the reported one.[24] Manganese perchlorate was reacted with ligand **1** in ethanol, and crystals of compound **2** were obtained by recrystallization from ethanol–dichloromethane. The resulting complex **2** was characterized by mass spectrometry, X-ray analysis, IR spectroscopy and elemental analysis.

Crystals of compound **2** are colorless at daylight and exhibit bright orange luminescence when exposed to UV light (Figure 1). It is known that the luminescence color of manganese complexes is related to their coordination sphere, and orange or red emission is related to the octahedral environment of the metal ion.[25–27] X-ray diffraction analysis confirmed that the coordination environment of Mn^{2+} in the crystal of **2** is a slightly distorted octahedron (Figure 2).[†] The symmetrically independent part of



Scheme 1

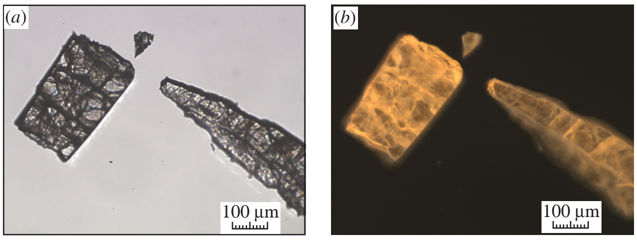


Figure 1 Micrographs of the crystals of **2** under (*a*) daylight and (*b*) UV light.

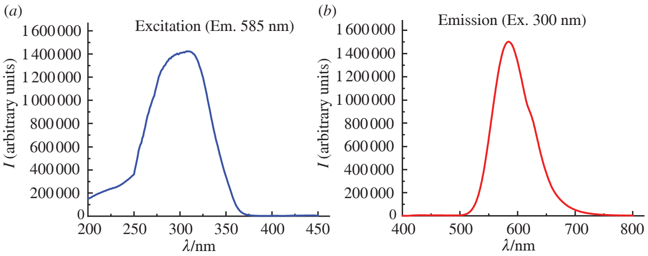


Figure 3 (*a*) Luminescence excitation at λ_{em} = 585 nm and (*b*) emission at λ_{ex} = 300 nm spectra of complex **2** in the solid state.

the crystal consists of a cationic Mn^{II} complex with three bidentate bis(diphenylphosphoryl)pyrrolidine ligands **1**, two perchlorate anions and a highly disordered ethanol molecule. The ligands are symmetrically arranged and form a ‘three-bladed propeller’ structure. Each ‘propeller’ consists of only one enantiomer of the ligand. The crystal packing of **2** is similar to the face-centered cubic packing, which may be explained by the high sphericity of the cation.

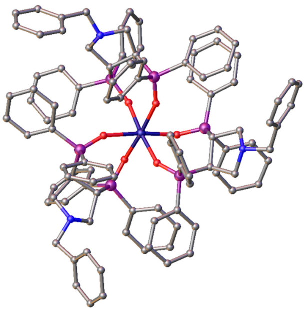


Figure 2 Molecular structure of complex **2**; C (grey), O (red), N (blue), P (purple), Mn (dark blue). Hydrogen atoms are omitted for clarity.

The luminescent properties of compound **2** were studied by steady-state and time-resolved luminescence spectroscopy. Figure 3 shows the luminescence excitation and emission spectra of **2** in the solid state. Upon excitation at 300 nm, the emission band with a maximum at 585 nm is observed. According to the literature, the emission of the complex is associated with the electronic transition $^4T_{1g}(^4G) \rightarrow {}^6A_{1g}(^6S)$ of Mn^{II} excited through the energy transfer from the ligand to the metal.[21,28–30] The excitation spectrum exhibits a single maximum at about 300 nm, which apparently corresponds to the $S_0 \rightarrow S_1$ ligand transition. The large gap between the excitation and emission maxima of the complex may be due to the large energy difference between the transitions of the ligand and manganese ion.[31,32] Complex **2** also demonstrates a high (60%) luminescence quantum yield in the solid state.

The luminescence decay kinetics of complex **2** was recorded using an excitation wavelength of 275 nm in the range of 480–720 nm. Figure 4 shows the kinetics at 580 nm (χ^2_{580} = 1.38). Upon excitation, the luminescence decay kinetics has a monoexponential character with a lifetime of 17.0 ms. The forbidden nature of the luminescence transitions leads to a long lifetime in the millisecond range. The χ^2_{glob} criterion of the global fitting procedure is 1.03.

We also aimed to study manganese complex based on a ligand containing an aliphatic substituent, obtained by the known method.[24] For this purpose, ligand **3** was introduced into a reaction with manganese perchlorate in ethanol and after 24 h of stirring the solvent was evaporated (Scheme 2). Unfortunately, complex **4** could not be separated from the initial reagents; numerous attempts of recrystallization were unsuccessful. Apparently, the presence of flexible *n*-hexyl substituent affects the crystallization ability of the complex.

Surprisingly, crystals of by-product **5** have precipitated from ethanol–dichloromethane mixture. X-ray analysis of these crystals revealed that the by-product is N-protonated ligand **3** bearing ClO_4^- counterion (Figure 5).[†]

In summary, a new luminescent manganese complex based on *N*-benzyl-3,4-bis(diphenylphosphoryl)pyrrolidine ligand exhibits valuable photophysical properties such as intense luminescence, a quantum yield of 60% and a luminescence lifetime of 17 ms. Analogous ligand containing *n*-hexyl substituent does not give crystalline manganese complex while the side reaction brings about an N-protonated ligand.

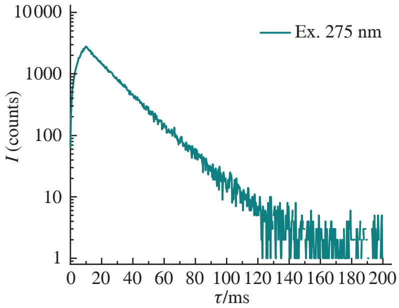


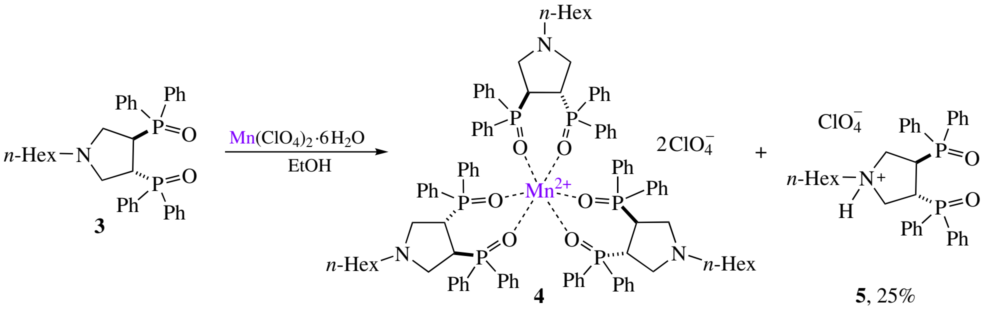
Figure 4 Luminescence decay of complex **2** at 580 nm (λ_{ex} = 275 nm).

[†] *Crystal data for* **2**. Crystals of $C_{106.75}H_{106}Cl_2MnN_3O_{15.75}P_6$ (*M* = 1994.60) are monoclinic, space group $P2_1/n$, at 100 K, *a* = 12.947(2), *b* = 26.217(4) and *c* = 29.364(6) Å, β = 98.626(6)°, *V* = 9854(3) Å^3, *Z* = 4, d_{calc} = 1.344 g cm^{-3}, μ(MoKα) = 0.353 mm^{-1}, *F*(000) = 4170. 87810 reflections were measured and 18046 independent reflections (R_{int} = 0.1811) were used in a further refinement. The refinement converged to wR_2 = 0.2695 and GOF = 1.024 for all independent reflections [R_1 = 0.0894 was calculated against *F* for 7541 observed reflections with $I > 2\sigma(I)$].

Crystal data for **5**. Crystals of $C_{34}H_{40}ClNO_6P_2$ (*M* = 656.06) are orthorhombic, space group $Pna2_1$, at 120 K, *a* = 10.9887(6), *b* = 39.023(2) and *c* = 22.7229(12) Å, β = 90°, *V* = 9743.8(9) Å^3, *Z* = 12, d_{calc} = 1.342 g cm^{-3}, μ(MoKα) = 0.262 mm^{-1}, *F*(000) = 4152. 85769 reflections were measured and 26157 independent reflections (R_{int} = 0.1963) were used in a further refinement. The refinement converged to wR_2 = 0.2284 and GOF = 0.980 for all independent reflections [R_1 = 0.0916 was calculated against *F* for 11287 observed reflections with $I > 2\sigma(I)$].

The measurements were made on a Bruker Smart Apex CCD diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by dual-space algorithm and refined in anisotropic approximation for non-hydrogen atoms against $F^2(hkl)$. Hydrogen atoms of methyl, methylene and aromatic fragments were calculated according to their idealized geometries and refined with constraints applied to C–H and N–H bond lengths and equivalent displacement parameters [$U_{eq}(H) = 1.2\,U_{eq}(X)$, X is a central atom of the XH_2 group; $U_{eq}(H) = 1.5\,U_{eq}(Y)$, Y is a central atom of the YH_3 group]. The structures were solved with the ShelXT program and refined with the ShelXL program. Molecular graphics was drawn using OLEX2 program. The solvent contribution to the structure factors in **2** and **5** was calculated and removed with Solvent Mask tool in OLEX2 program.

CCDC 2367307 (**2**) and 2367308 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.



5, 25%

4

(estimated structure, was not isolated)

Scheme 2

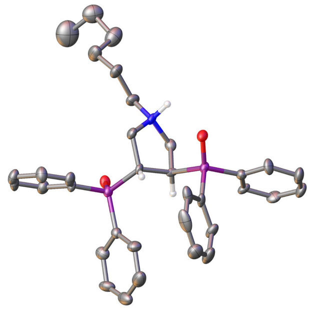


Figure 5 Molecular structure of salt **5** presented as ADP ellipsoids at 50% probability; C (grey), H (white), O (red), N (blue), P (purple). Some hydrogen atoms are omitted for clarity.

This study was supported by the Russian Science Foundation (grant no. 20-13-00329). Characterization of compounds by NMR, IR spectroscopy, mass spectrometry and X-ray analysis were performed with financial support from the Ministry of Science and Higher Education of the Russian Federation (agreement no. 075-00277-24-00) using the equipment of the Center for Molecular Composition Studies of INEOS RAS. The luminescence quantum yield and lifetime measurements were performed using the equipment of the Shared Research Center 'Structural diagnostics of materials' of NRC 'Kurchatov institute' within the State assignment of NRC 'Kurchatov institute'.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7577.

References

1 Y. Qin, P. She, X. Huang, W. Huang and Q. Zhao, *Coord. Chem. Rev.*, 2020, **416**, 213331; https://doi.org/10.1016/j.ccr.2020.213331.

2 E. Song, S. Ye, T. Liu, P. Du, R. Si, X. Jing, S. Ding, M. Peng, Q. Zhang and L. Wondraczek, *Adv. Sci.*, 2015, **2**, 1500089; https://doi.org/10.1002/advs.201500089.

3 A. Harriman, *Coord. Chem. Rev.*, 1979, **28**, 147; https://doi.org/10.1016/S0010-8545(00)82012-3.

4 P. She, Y. Ma, Y. Qin, M. Xie, F. Li, S. Liu, W. Huang and Q. Zhao, *Matter*, 2019, **1**, 1644; https://doi.org/10.1016/j.matt.2019.08.016.

5 G.-H. Tan, Y.-N. Chen, Y.-T. Chuang, H.-C. Lin, C.-A. Hsieh, Y.-S. Chen, T.-Y. Lee, W.-C. Miao, H.-C. Kuo, L.-Y. Chen, K.-T. Wong and H.-W. Lin, *Small*, 2023, **19**, 1; https://doi.org/10.1002/smll.202205981.

6 S. Yan, K. Tang, Y. Lin, Y. Ren, W. Tian, H. Chen, T. Lin, L. Qiu, X. Pan and W. Wang, *ACS Energy Lett.*, 2021, **6**, 1901; https://doi.org/10.1021/acsenergylett.1c00250.

7 Q. Zhou, L. Dolgov, A. M. Srivastava, L. Zhou, Z. Wang, J. Shi, M. D. Dramićanin, M. G. Brik and M. Wu, *J. Mater. Chem. C*, 2018, **6**, 2652; https://doi.org/10.1039/c8tc00251g.

8 Z. Zhou, H. Meng, F. Li, T. Jiang, Y. Yang, S. Liu and Q. Zhao, *Inorg. Chem.*, 2023, **62**, 5729; https://doi.org/10.1021/acs.inorgchem.3c00273.

9 Z. Zhou, T. Jiang, Y. Yang, Y. Deng, M. Wang, Y. Ma, S. Liu and Q. Zhao, *Adv. Opt. Mater.*, 2024, **12**, 302185; https://doi.org/10.1002/adom.202302185.

10 H. Peng, T. Huang, B. Zou, Y. Tian, X. Wang, Y. Guo, T. Dong, Z. Yu, C. Ding, F. Yang and J. Wang, *Nano Energy*, 2021, **87**, 106166; https://doi.org/10.1016/j.nanoen.2021.106166.

11 Y. Wu, X. Zhang, L.-J. Xu, M. Yang and Z.-N. Chen, *Inorg. Chem.*, 2018, **57**, 9175; https://doi.org/10.1021/acs.inorgchem.8b01205.

12 A. S. Berezin, K. A. Vinogradova, V. A. Nadolinny, T. S. Sukhikh, V. P. Krivopalov, E. B. Nikolaenkova and M. B. Bushuev, *Dalton Trans.*, 2018, **47**, 1657; https://doi.org/10.1039/c7dt04535b.

13 X. Huang, Y. Qin, P. She, H. Meng, S. Liu and Q. Zhao, *Dalton Trans.*, 2021, **50**, 8831; https://doi.org/10.1039/d1dt00914a.

14 M. Bortoluzzi, J. Castro, F. Enrichi, A. Vomiero, M. Busato and W. Huang, *Inorg. Chem. Commun.*, 2018, **92**, 145; https://doi.org/10.1016/j.inoche.2018.04.023.

15 P. She, Z. Zheng, Y. Qin, F. Li, X. Zheng, D. Zhang, Z. Xie, L. Duan and W.-Y. Wong, *Adv. Opt. Mater.*, 2024, **12**, 2302132; https://doi.org/10.1002/adom.202302132.

16 M. Bortoluzzi, J. Castro, A. Gobbo, V. Ferraro, L. Pietrobon and S. Antoniutti, *New J. Chem.*, 2020, **44**, 571; https://doi.org/10.1039/C9NJ05083C.

17 Y. Wu, X. Zhang, Y.-Q. Zhang, M. Yang and Z.-N. Chen, *Chem. Commun.*, 2018, **54**, 13961; https://doi.org/10.1039/c8cc08665f.

18 Y. Qin, P. Tao, L. Gao, P. She, S. Liu, X. Li, F. Li, H. Wang, Q. Zhao, Y. Miao and W. Huang, *Adv. Opt. Mater.*, 2019, **7**, 1801160; https://doi.org/10.1002/adom.201801160.

19 A. V. Artem'ev, A. S. Berezin, V. K. Brel, V. P. Morgalyuk and D. G. Samsonenko, *Polyhedron*, 2018, **148**, 184; https://doi.org/10.1016/j.poly.2018.04.012.

20 M. P. Davydova, I. A. Bauer, V. K. Brel, M. I. Rakhmanova, I. Yu. Bagryanskaya and A. V. Artem'ev, *Eur. J. Inorg. Chem.*, 2020, 695; https://doi.org/10.1002/ejic.201901213.

21 A. S. Berezin, D. G. Samsonenko, V. K. Brel and A. V. Artem'ev, *Dalton Trans.*, 2018, **47**, 7306; https://doi.org/10.1039/C8DT01041B.

22 Y.-Y. Tang, Z.-X. Wang, P.-F. Li, Y.-M. You, A. Stroppa and R.-G. Xiong, *Inorg. Chem. Front.*, 2017, **4**, 154; https://doi.org/10.1039/C6QI00148C.

23 A. S. Berezin, M. P. Davydova, I. Yu. Bagryanskaya, O. I. Artyushin, V. K. Brel and A. V. Artem'ev, *Inorg. Chem. Commun.*, 2019, **107**, 107473; https://doi.org/10.1016/j.inoche.2019.107473.

24 Y. N. Kononevich, A. D. Volodin, A. A. Korlyukov, V. K. Brel and A. M. Muzafarov, *Mendeleev Commun.*, 2024, **34**, 51; https://doi.org/10.1016/j.mencom.2024.01.015.

25 J. Lin, L. Wang, Q. Zhang, F. Bu, T. Wu, X. Bu and P. Feng, *J. Mater. Chem. C*, 2016, **4**, 1645; https://doi.org/10.1039/C5TC04191K.

26 J. Lin, Q. Zhang, L. Wang, X. Liu, W. Yan, T. Wu, X. Bu and P. Feng, *J. Am. Chem. Soc.*, 2014, **136**, 4769; https://doi.org/10.1021/ja501288x.

27 J. Orive, J. L. Mesa, R. Balda, J. Fernández, J. Rodriguez Fernández, T. Rojo and M. I. Arriortua, *Inorg. Chem.*, 2011, **50**, 12463; https://doi.org/10.1021/ic201226t.

28 M. Bortoluzzi, J. Castro, E. Trave, D. Dallan and S. Favaretto, *Inorg. Chem. Commun.*, 2018, **90**, 105; https://doi.org/10.1016/j.inoche.2018.02.018.

29 L. E. Orgel, *J. Chem. Phys.*, 1955, **23**, 1958; https://doi.org/10.1063/1.1740614.

30 H.-Y. Ye, Q. Zhou, X. Niu, W.-Q. Liao, D.-W. Fu, Y. Zhang, Y.-M. You, J. Wang, Z.-N. Chen and R.-G. Xiong, *J. Am. Chem. Soc.*, 2015, **137**, 13148; https://doi.org/ 10.1021/jacs.5b08290.

31 S. H. Linwood and W. A. Weyl, *J. Opt. Soc. Am.*, 1942, **32**, 443; https://doi.org/10.1364/JOSA.32.000443.

32 J. I. Zink, G. E. Hardy and G. Gliemann, *Inorg. Chem.*, 1980, **19**, 488; https://doi.org/10.1021/ic50204a041.

Received: 23rd July 2024; Com. 24/7577