

Dithiolanes and Oxathiolanes Obtained from Cymantrene Derivatives: Synthesis and Properties

Lyudmila N. Telegina,^{*[a]} Tatyana V. Strelkova,^[a] Mariam G. Ezernitskaya,^[a] Vladimir G. Alekseev,^[b] Aleksander F. Smol'yakov,^[a, c] and Elena S. Kelbysheva^[a]

Novel cymantrene derivatives containing dithiolane and oxathiolane five-membered cycles were prepared. Their spectral, optical, and redox properties were investigated by NMR, IR, UV-vis spectroscopy, and CV. Under the conditions of irradiation and subsequent dark reaction, the effect of ligand exchange on physicochemical properties was studied. Photolysis of tricarbonyl complexes leads to the formation of rare, stable four-

1. Introduction

Dithiolanes and oxathiolanes are important classes of compounds that are widely used in various fields. Thioacetal and thioketal groups are mainly used as protecting groups for carbonyl derivatives.^[1-5] Thioacetals are precursors or intermediates in the preparation of difficult to obtain classes of sulfur-containing compounds, such as thiocyanothioesters,^[6] disulfide-linked-dithioesters,^[7] substituted ketene diothi(ol)anes,^[8] and so forth. Thiolanes behave specifically when interacting with various metals and their derivatives. The main process of complex formation is the opening of the dithiolane ring. In particular, an efficient method for the preparation of Ru-dithiolate alkylidene complexes starting from cyclic thioacetals was reported, resulting in Ru-synthon in good yield.^[9] The reaction of thioacetal with Ru(cod)(cot) or $Ru(PPh_3)_3(H)_2$ lead to the elimination of the carbonyl compound and the metal atom formed S-Ru-S bond. However, in a number of cases, ruthenium forms complexes without ring opening with one of the sulfur atoms.^[10] Since thioacetals form complexes with a wide range of metals, effective fluorescent chemosensors for metal ions, such as Hg²⁺, were created on

 [a] Dr. L. N. Telegina, Dr. T. V. Strelkova, Dr. M. G. Ezernitskaya, Dr. A. F. Smol'yakov, Dr. E. S. Kelbysheva A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova 28, Moscow 119334, Russia E-mail: popova-ln@mail.ru

- [b] Dr. V. G. Alekseev Faculty of Chemistry and Technology, Tver State University, Zhelyabova 33, Tver 170100, Russia
- [c] Dr. A. F. Smol'yakov Plekhanov Russian University of Economics, Stremyanny per. 36, Moscow 117997. Russia
- Supporting information for this article is available on the WWW under https://doi.org/10.1002/slct.202404224

membered chelate complexes with Mn—S bond, one of which has been successfully isolated and characterized by X-ray. However, in the presence of a competitive external ligand (L), the Mn—S bond dissociated, followed by the formation of new dicarbonyl complexes with the Mn—L bond, that shows the hemilabile nature of the Mn—S bond in chelate complexes.

their basis.^[11-14] The process of recognition by such probes is carried out using a chemical reaction between the sensor and the detection object with the formation of photoactive compounds having a different structure, which leads to a change in spectral properties and allows for the implementation of optical detection of metal ions. The advantage of such probes is the stability of the resulting complexes and the ability to maintain the detection signal for a long time. Ferrocenated thiols and bis-dithianes were obtained and described,^[15] which were unique detectors for ions of various metals. In this work, we did not describe the mechanism of metal recognition by thioacetal derivatives, in connection with which the question remains whether the opening of the thioacetal ring occurs during complex formation. However, it was shown that the ferrocenyl derivative of dithiolane can act as a ligand and form a complex with copper without opening the thiolane ring.^[16]

It is known that cymantrene (cyclopentadienyl tricarbonyl manganese, (C₅H₅)Mn(CO)₃) is a unique half-sandwich compound capable of entering into ligand exchange reactions and forming coordination complexes with various donor ligands.^[17–18] Photolysis of cymantrene derivatives, in the side chain of which there are fragments capable of coordination with the manganese atom, can lead to the formation of chelate dicarbonyl complexes with different thermodynamic and kinetic stability. We previously showed that sulfur-containing derivatives of cymantrene, as a result of photolysis leading to dissociation of the CO ligand, form thermodynamically stable and kinetically hemilabile in solutions coordination four-membered chelate complexes.^[19] The changes in spectral and electrochemical properties were observed. In this regard, we obtain a series of dithiolane and oxathiolane derivatives of cymantrene (Scheme 1), in which the sulfur atom is located in the 2 position of the side chain, and study their photochemical behavior using IR, NMR, UV spectroscopy, and CV.



Acknowledgements

This work was supported by the Ministry of Science and Higher Education of the Russian Federation (Contract/Agreement No. 075-00277-24-00).

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: 4-Membered chelates · Cymantrene · Ligand exchange · Photochemistry · Thiolane

- [1] B. Roy, J. Sulfur Chem. 2023, 44, 779-813.
- [2] C. M. B. K. Kourra, N. Cramer, Chem. Sci. 2016, 7, 7007–7012.
- [3] S. Naik, R. Gopinath, M. Goswami, B. K. Patel, Org. Biomol. Chem. 2004, 2, 1670–1677.
- [4] M. H. Ali, M. G. Gomes, Synthesis 2005, 2005, 1326–1332.
- [5] H. Adibi, H. A. Samimi, N. Iranpoor, Chin. J. Chem. 2008, 26, 2086–2092.
- [6] P. D. Dharpure, M. Behera, V. V. Khade, A. S. Thube, R. G. Bhat, Org. Lett. 2022, 24, 6919–6924.
 [7] a) B. G. Bhat, P. D. Dharpure, M. Bohorp, A. S. Thuba, Chambridge, Chambridge,
- [7] a) R. G. Bhat, P. D. Dharpure, M. Behera, A. S. Thube, *ChemRxiv* preprint, **2021**, https://doi.org/10.26434/chemrxiv-2021-x9kht; b) P. D. Dharpure, M. Behera, A. S. Thube, R. G. Bhat, *Chem. Asian J.* **2023**, *18*, e202201128.

- [8] Y.-C. Huang, A. Nguyen, S. Gräßle, S. Vanderheiden, N. Jung, *Beilstein J. Org. Chem.* 2018, 14, 515–522.
- [9] A. M. McKinty, D. W. Stephan, Dalton Trans. 2014, 43, 2710-2712.
- [10] G. Segalovich-Gerendash, M. Baranov, N. G. Lemcoff, R. S. Phatake, Organometallics 2023, 42, 825–831.
- [11] Y. Gao, T. Ma, Z. Ou, W. Cai, G. Yang, Y. Li, M. Xu, Q. Li, *Talanta* 2018, 178, 663–669.
- [12] X. Dai, Y. Li, Y. Sun, Z. Li, J. Tao, L. Qu, R. Yang, Sens. Actuators, B 2023, 392, 134104.
- [13] Y. Gu, R. Jia, Y. Yu, S. Li, J. Zhu, X. Feng, Y. Lu, ACS Appl. Mater. Interfaces 2024, 16, 10805–10812.
- [14] P. Piyanuch, S. Aryamueang, T. Khrootkaew, K. Mahingsadet, K. Chansaenpak, A. Kamkaew, Spectrochim. Acta, Part A 2024, 317, 124429.
- [15] A. K. Srivastava, Y. Upadhyay, M. Ali, S. K. Sahoo, R. K. Joshi, J. Organomet. Chem. 2020, 920, 121318.
- [16] A. Raghuvanshi, N. J. Dargallay, M. Knorr, L. Viau, L. Knauer, C. Strohmann, J. Inorg. Organomet. Polym. 2017, 27, 1501–1513.
- [17] A. A. Grineva, N. Lugan, D. A. Valyaev, in *Manganese Catalysis in Organic Synthesis* (Ed: J.-B. Sortais), Wiley-VCH GmbH, Germany, 2021.
- [18] E. S. Kelbysheva, T. V. Strelkova, M. G. Ezernitskaya, Y. A. Borisov, A. F. Smol'yakov, A. N. Rodionov, L. N. Telegina, J. Organomet. Chem. 2022, 979, 122496.
- [19] E. S. Kelbysheva, M. G. Ezernitskaya, T. V. Strelkova, Y. A. Borisov, L. N. Telegina, *ChemistrySelect* **2021**, *6*, 9861–9866.
- [20] J. W. Kee, Y. Y. Tan, B. H. G. Swennenhuis, A. A. Bengali, W. Y. Fan, Organometallics 2011, 30, 2154–2159.
- [21] J. W. Kee, T. S. Chwee, X. Y. Tan, R. D. Webster, W. Y. Fan, Organometallics 2013, 32, 4359–4365.
- [22] A. Kostyuchenko, A. Kurowska, P. Zassowski, T. Y. Zheleznova, E. B. Ulyankin, W. Domagala, A. Pron, A. S. Fisyuk, J. Org. Chem. 2019, 84, 10040–10049.
- [23] N. M. Loim, M. A. Kondratenko, V. I. Sokolov, J. Org. Chem. 1994, 59, 7485–7487.
- [24] C. M. Cortis, J.-M. Langlois, M. D. Beachy, R. A. Friesner, J. Chem. Phys. 1996, 105, 5472–5484.
- [25] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Crystallogr. 2009, 42, 339–341.
- [26] G. M. Sheldrick, Acta Crystallogr., Sect. A:Found. Adv. 2015, 71, 3-8.
- [27] G. M. Sheldrick, Acta Crystallogr., Sect. A:Found. Adv. 2008, 64, 112-122.

Manuscript received: September 03, 2024