Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2022, **32**, 585–587

Mendeleev Communications

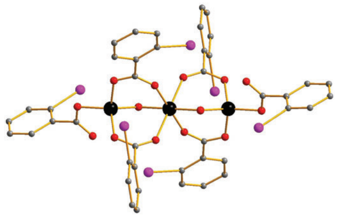
Bi- or trinuclear 2-iodobenzoate complexes of Zn^{II}: crystal structures and luminescence

Mikhail A. Bondarenko,[a] Marianna I. Rakhmanova,[a] Alexander S. Novikov,[b] Maxim N. Sokolov[a] and Sergey A. Adonin*[a]

[a] *A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: adonin@niic.nsc.ru*
[b] *Institute of Chemistry, St. Petersburg State University, 199034 St. Petersburg, Russian Federation*

DOI: 10.1016/j.mencom.2022.09.005

Reactions of zinc nitrate with 2-iodobenzoic acid (2-IBA) and different pyridines result in binuclear Zn^{II} carboxylate complexes $[Zn_2(2\text{-IBA})_4L_2]$, where L = Py, 3-MePy and $3,5\text{-}Me_2Py$, while in the case of $2,4,6\text{-}Me_3Py$, trinuclear $(2,4,6\text{-}Me_3PyH)_2[Zn_3(2\text{-IBA})_6(OH)_2]$ is formed.



Keywords: zinc, carboxylates, non-covalent interactions, crystal structure, luminescence.

Among the great variety of coordination compounds, carboxylate complexes represent a ‘classical’ area which continues attracting attention of researchers.[1–6] From the viewpoint of structural chemistry, this class is very attractive because of its enormous diversity: there are discrete mono- and polynuclear[7–10] complexes, sometimes containing dozens of metal atoms,[11–16] as well as coordination polymers (including MOFs[5,6,17–19]); heterometallic carboxylates are known as well.[2,20–22] Non-covalent interactions (*e.g.*, hydrogen bonding and stacking) play very important role in self-organization of these compounds: apart of crystal packing, those can induce assembly of certain coordination units. On the other hand, supramolecular contacts are responsible for numerous useful physical properties (such as sensing, especially for MOFs). For this reason, it is not wondering that ability of metal carboxylates to be involved in ‘non-classical non-covalent interactions’ – halogen (XB), chalcogen and pnictogen bonding – represents an interesting research task which is on focus of current research. Recent works demonstrate[23–27] that even relatively simple halogen-substituted arenecarboxylates (such as, for example, 4-iodobenzoates) can readily form XB in solid state. Very recently, we showed[28] that 2-iodobenzoate complexes of Cu^{II} can reveal the same feature. Continuing this work, we decided to investigate behaviour of Zn^{II} 2-iodobenzoate (2-IBA) complexes which, to our best knowledge, were unknown yet (our first work on this topic was published last year[29]).

Hereby we present four new Zn^{II} complexes – binuclear $[Zn_2(2\text{-IBA})_4L_2]$ [L = Py (**1**), 3-MePy (**2**) and $3,5\text{-}Me_2Py$ (**3**)] and $(2,4,6\text{-}Me_3PyH)_2[Zn_3(2\text{-IBA})_6(OH)_2]$ (**4**) [see Online Supplementary Materials (SI) for synthetic details]. Synthetic procedures for **1** and **2** are given in SI. According to XRD,[†] **1–3** belong to the paddlewheel structural type (Figure 1), which is one of the most common[30–32] in chemistry of carboxylate complexes (according to CSD data, there are over 1600 structures for M = Cu^{II} and about 200 for M = Zn^{II}). The Zn···Zn, Zn–O and Zn–N distances are listed in Table 1; overall, these data agree well with those found in other binuclear Zn^{II} carboxylates.

[†] *Crystal data for* **1**. $C_{38}H_{26}I_4N_2O_8Zn_2$ (M = 1276.95), monoclinic, $P2_1/c$, a = 10.7465(4), b = 15.3117(5) and c = 23.6517(8) Å, β = 95.121(3)°, V = 3876.3(2) Å^3, Z = 4, μ(MoKα) = 4.48 mm^{-1}. Total of 19519 reflections were collected, and 7353 independent reflections (R_{int} = 0.026) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.028, wR_2 = 0.059, GoF = 1.02.

Crystal data for **2**. $C_{40}H_{30}I_4N_2O_8Zn_2$ (M = 1305.00), monoclinic, $P2_1/c$, a = 10.4789(5), b = 21.4721(10) and c = 9.5766(4) Å, β = 97.893(4)°, V = 2134.36(17) Å^3, Z = 2, μ(MoKα) = 4.07 mm^{-1}. Total of 9830 reflections were collected, and 4052 independent reflections (R_{int} = 0.024) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.030, wR_2 = 0.068, GoF = 1.03.

Crystal data for **3**. $C_{42}H_{34}I_4N_2O_8Zn_2$ (M = 1333.05), monoclinic, space group $P2_1/n$, a = 3.9466(7), b = 11.0012(6) and c = 14.7094(8) Å, β = 105.402(6)°, V = 2175.8(2) Å^3, Z = 2, μ(MoKα) = 3.99 mm^{-1}. Total of 10647 reflections were collected, and 4129 independent reflections (R_{int} = 0.027) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.027, wR_2 = 0.062, GoF = 1.08.

Crystal data for **4**. $C_{58}H_{50}I_6N_2O_{14}Zn_3$ (M = 1956.51), triclinic, space group $P\bar{1}$, a = 11.0413(2), b = 12.4026(2) and c = 12.7793(3) Å, α = 111.367(2)°, β = 91.582(2)°, γ = 100.367(2)°, V = 1594.80(6) Å^3, Z = 1, μ(MoKα) = 4.09 mm^{-1}. Total of 12896 reflections were collected, and 6066 independent reflections (R_{int} = 0.025) were used in the further refinement. Final R indexes [$I > 2\sigma(I)$]: R_1 = 0.032, wR_2 = 0.068, GoF = 1.04.

The data were collected at 150 (**1**, **3**, **4**) or 140 K (**2**) on an Agilent Xcalibur diffractometer with an area AtlasS2 detector [graphite monochromator, μ(MoKα) = 0.71073 Å, ω-scans]. Absorption correction was applied by CrysAlisPro program package (CrysAlisPro 1.171.38.41, Rigaku Oxford Diffraction: The Woodlands, TX, USA, 2015). The crystal structures were solved using the SHELXT[54] and refined using SHELXL[55] programs. Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model.

CCDC 2155379–2155382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

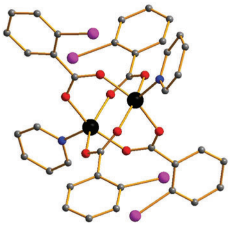


Figure 1 Structure of **1**. Here and below: Zn black, C grey, N blue, O red, I purple, H atoms are omitted for clarity.

Table 1 Selected distances in the structures **1**–**3** (Å).

Complex	Zn–O	Zn–N	Zn···Zn
1	2.020(2)–2.091(2)	2.029(3)–2.030(3)	3.0125(5)
2	2.023(3)–2.052(3)	2.027(3)	2.9645(8)
3	2.028(2)–2.072(2)	2.020(3)	2.9725(7)

Table 2 The quantum yields [PL QY (%)], emission decay times (τ) for the complexes **1**–**4**, CIE chromaticity coordinate recorded for the solid state at 300 K.

Complex	PL QY (%) (λ_{ex} = 380 nm)	Decay time τ/ns (λ_{ex} = 350 nm)	CIE coordinate (x; y)
1	2.2	$t_1 = 2$, $t_2 = 10$	(0.209; 0.221)
2	2.5	$t_1 = 3$, $t_2 = 11$	(0.219; 0.245)
3	3.1	$t_1 = 1$, $t_2 = 5$	(0.214; 0.250)
4	4.2	$t_1 = 2$, $t_2 = 10$	(0.249; 0.303)

As follows from XRD data, the I···I and I···O distances in **1** and **3** exceed the sum of Bondi's van der Waals radii (3.98 and 3.50 Å, respectively[33]). In **2**, there are I···I contacts [3.7867(4) Å] involving all four 2-IBA ligands (Figure 2), but their geometries (C–I–I is 141.09–154.06°) correspond to so-called Type I halogen···halogen interactions (packing-induced, not 'true halogen bonding').

The use of more sterically hindered pyridine (2,4,6-collidine) results in formation of **4** belonging to different, less common structural type. In its structure, there are $[Zn_3(2\text{-IBA})_6(OH)_2]^{2-}$ anions (Figure 3). Coordination environment of the central Zn is octahedral; it consists of two μ_2-hydroxo ligands (Zn–O = 2.038 Å) and four μ_2-carboxylates [Zn–O = = 2.078(2)–2.174(3) Å]. The neighboring Zn are tetrahedral [$Zn–O_{OH}$ = 1.954(3) Å, $Zn–O_{COO}$ = 1.963(2)–1.976(3) Å]; two 2-IBA are coordinated in monodentate mode [the longer Zn···O distances are 2.712 Å; as it was previously shown by us,[34] DFT calculations demonstrate the absence of bond critical points (3, –1) in such cases. The $2,4,6\text{-}Me_3PyH^+$ cations form relatively short [1.778(2) Å] hydrogen bond with μ_2-OH. Although the $\{Zn_3(RCOO)_n\}$ pattern is not uncommon, there are few compounds revealing close structural similarity: there is only one example with μ_2-hydroxo ligands;[35] the number of $\{Zn_3(RCOO)_6\}$ complexes is only slightly higher.[36–43]

To investigate the nature and quantify the strengths of hypothetic noncovalent interactions I···I and I···O in solid state in **1**–**4**, we performed DFT calculations and topological analysis of the electron density distribution within the QTAIM approach[44] (see SI for details; this approach was extensively used by us earlier[45–48]). Results of QTAIM analysis summarized in Table S2 and graphically presented in Figures S1–S4 (SI; including visualization of electron localization functions). Most surprising fact is that QTAIM analysis reveals the presence of bond critical points (3, –1) for noncovalent interactions I···I and I···O in all structures – even in the cases where corresponding distances exceed not only Bondi's, but also Alvarez[49] van der Waals radii. The energies[50] of such interactions are not high (1.7 kcal mol^{-1} for **1**, 0.9 kcal mol^{-1} for **3** and **4**, see Table 3), but calculations confirm their presence unambiguously. Also, as follows from the sign of λ_2 (it is <0 in all cases), these interactions are attractive.[51,52] Hirshfeld surface analysis performed for **1**–**4** indicates (see SI, Figure S5) that H···H and C···H interatomic contacts give the major contributions to crystal packings.

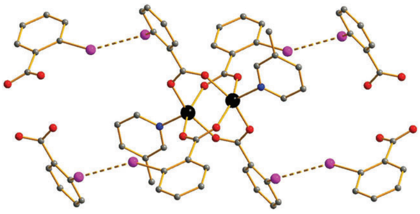


Figure 2 I···I interactions (dashed) in the structure of **2**.

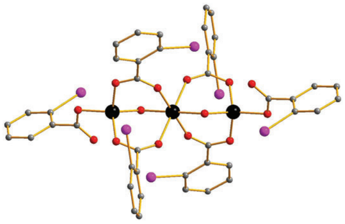


Figure 3 Structure of $[Zn_3(2\text{-IBA})_6(OH)_2]^{2-}$ anions in **4**.

As follows from PXRD data (see SI), **1**–**4** were isolated as single phases. The solid state photoluminescent spectra of **1**–**4** measured at room temperature are shown in SI (Figure S6). The main emission peaks of complex **1**–**3** were observed at 420, 440 and 460 nm (λ_{ex} = 380 nm). The fluorescence bands in **1**–**3** are due to intra-ligand π–π* transition. The emission of **4** shows a small red shift as compared to **1**–**3**, which can be explained by the difference in π-stacking between the aromatic rings of different [Zn(L)] units. It is reasonable to assume that ligand-centered (LC) and/or ligand-to-ligand charge transfer (LLCT) processes are responsible for the luminescence properties.[53] This is also in line with the measured lifetimes of the excited states, which are in nanosecond range (Table 2). The quantum yields (QY) are in 2.2–4.2% range. The resultant emission colors at λ_{ex} = 380 nm, as displayed on CIE 1931 chromaticity diagrams (Figure S6, SI), are blue for **1**–**3** and blue-green for **4**.

This work was supported by Russian Foundation for Basic Research (Grant No. 19-43-540005) and, in part, by the Ministry of Science and Higher Education of the Russian Federation (structural characterization of the samples, 121031700313-8).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.09.005.

References

1 S. A. Nikolaevskii, M. A. Kiskin, A. G. Starikov, N. N. Efimov, A. S. Bogomyakov, V. V. Minin, E. A. Ugolkova, O. M. Nikitin, T. V. Magdesieva, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2019, **45**, 273 (*Koord. Khim.*, 2019, **45**, 219).

2 M. A. Shmelev, N. V. Gogoleva, D. A. Makarov, M. A. Kiskin, I. A. Yakushev, F. M. Dolgushin, G. G. Aleksandrov, E. A. Varaksina, I. V. Taidakov, E. V. Aleksandrov, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2020, **46**, 1 (*Koord. Khim.*, 2020, **46**, 3).

3 S. A. Nikolaevskii, D. S. Yambulatov, A. A. Starikova, A. A. Sidorov, M. A. Kiskin and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2020, **46**, 260 (*Koord. Khim.*, 2020, **46**, 241).

4 E. N. Zorina-Tikhonova, D. S. Yambulatov, M. A. Kiskin, E. S. Bazhina, S. A. Nikolaevskii, N. V. Gogoleva, I. A. Lutsenko, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2020, **46**, 75 (*Koord. Khim.*, 2020, **46**, 67).

5 A. A. Sapianik, E. R. Dudko, D. G. Samsonenko and V. P. Fedin, *J. Struct. Chem.*, 2020, **61**, 1957.

6 A. A. Sapianik, E. N. Zorina-Tikhonova, M. A. Kiskin, D. G. Samsonenko, K. A. Kovalenko, A. A. Sidorov, I. L. Eremenko, D. N. Dybtsev, A. J. Blake, S. P. Argent, M. Schröder and V. P. Fedin, *Inorg. Chem.*, 2017, **56**, 1599.

7 N. V. Gogoleva, M. A. Shmelev, I. S. Evstifeev, S. A. Nikolaevskii, G. G. Aleksandrov, M. A. Kiskin, Z. V. Dobrokhotova, A. A. Sidorov and I. L. Eremenko, *Russ. Chem. Bull.*, 2016, **65**, 181.

8 N. V. Gogoleva, G. G. Aleksandrov, A. A. Pavlov, M. A. Kiskin, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2018, **44**, 91 (*Koord. Khim*., 2018, **44**, 3).

9 A. E. Goldberg, M. A. Kiskin, S. A. Nikolaevskii, E. N. Zorina-Tikhonova, G. G. Aleksandrov, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2015, **41**, 182 (*Koord. Khim*., 2015, **41**, 163).

10 I. A. Lutsenko, M. A. Kiskin, S. A. Nikolaevskii, Yu. V. Nelyubina, P. V. Primakov, A. S. Goloveshkin, V. K. Imshennik, Yu. V. Maksimov, A. A. Sidorov and I. L. Eremenko, *Mendeleev Commun.*, 2020, **30**, 273.

11 E. N. Zorina-Tikhonova, A. V. Vologzhanina, K. A. Babeshkin, N. N. Efimov, P. V. Dorovatovskii, M. A. Kiskin, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2021, **47**, 180 (*Koord. Khim*., 2021, **47**, 153).

12 K. N. Pantelis, P. S. Perlepe, S. Grammatikopoulos, C. Lampropoulos, J. Tang and T. C. Stamatatos, *Molecules*, 2020, **25**, 2191.

13 J. Pasán, A. B. Lago, L. Cañadillas-Delgado, Ó. Fabelo, C. Ruiz-Pérez, F. Lloret and M. Julve, *Polyhedron*, 2019, **170**, 217.

14 A. Abhervé, M. J. Recio-Carretero, M. López-Jordá, J. M. Clemente-Juan, J. Canet-Ferrer, A. Cantarero, M. Clemente-León and E. Coronado, *Inorg. Chem.*, 2016, **55**, 9361.

15 V. Chandrasekhar, R. K. Metre and D. Sahoo, *Eur. J. Inorg. Chem.*, 2014, **2014**, 164.

16 D. I. Alexandropoulos, E. E. Moushi, C. Papatriantafyllopoulou, C. M. Beavers, S. J. Teat, A. J. Tasiopoulos, G. Christou and T. C. Stamatatos, *Polyhedron*, 2016, **108**, 131.

17 M. O. Barsukova, D. G. Samsonenko, A. A. Sapianik, S. A. Sapchenko and V. P. Fedin, *Polyhedron*, 2018, **144**, 219.

18 A. A. Sapianik, M. A. Kiskin, D. G. Samsonenko, A. A. Ryadun, D. N. Dybtsev and V. P. Fedin, *Polyhedron*, 2018, **145**, 147.

19 S. L.-F. Chan, S. Gao, S. S.-Y. Chui, L. Shek, J.-S. Huang and C.-M. Che, *Chem. – Eur. J.*, 2012, **18**, 11228.

20 A. A. Sidorov, M. A. Kiskin, G. G. Aleksandrov, N. V. Gogoleva, S. A. Nikolaevskii and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2016, **42**, 621 (*Koord. Khim*., 2016, **42**, 581).

21 I. P. Stolarov, N. V. Cherkashina, I. A. Yakushev, A. V. Churakov, A. B. Kornev and E. V. Fatyushina, *Russ. J. Inorg. Chem.*, 2020, **65**, 507 (*Zh. Neorg. Khim*., 2020, **65**, 487).

22 M. A. Shmelev, N. V. Gogoleva, F. M. Dolgushin, K. A. Lyssenko, M. A. Kiskin, E. A. Varaksina, I. V. Taidakov, A. A. Sidorov and I. L. Eremenko, *Russ. J. Coord. Chem.*, 2020, **46**, 493 (*Koord. Khim*., 2020, **46**, 437).

23 M. V. Chernysheva, M. Bulatova, X. Ding and M. Haukka, *Cryst. Growth Des.*, 2020, **20**, 7197.

24 A. D. Burrows, M. F. Mahon, P. R. Raithby, A. J. Warren, S. J. Teat and J. E. Warren, *CrystEngComm*, 2012, **14**, 3658.

25 L. Brammer, G. M. Espallargas and S. Libri, *CrystEngComm*, 2008, **10**, 1712.

26 P. Smart, Á. Bejarano-Villafuerte, R. M. Hendry and L. Brammer, *CrystEngComm*, 2013, **15**, 3160.

27 Y. V. Torubaev and I. V. Skabitsky, *CrystEngComm*, 2020, **22**, 6661.

28 S. A. Adonin, M. A. Petrov, P. A. Abramov, A. S. Novikov, M. N. Sokolov and V. P. Fedin, *Polyhedron*, 2019, **171**, 312.

29 M. A. Bondarenko and S. A. Adonin, *J. Struct. Chem.*, 2021, **62**, 1251.

30 M. Iqbal, S. Ali and M. N. Tahir, *Z. Anorg. Allg. Chem.*, 2018, **644**, 172.

31 N. W. Attandoh, S. O. Ojwach and O. Q. Munro, *Eur. J. Inorg. Chem.*, 2014, 3053.

32 P. Smart, Á. Bejarano-Villafuerte and L. Brammer, *CrystEngComm*, 2013, **15**, 3151.

33 A. Bondi, *J. Phys. Chem.*, 1966, **70**, 3006.

34 M. A. Bondarenko, M. I. Rakhmanova, P. E. Plyusnin, P. A. Abramov, A. S. Novikov, K. Rajakumar, M. N. Sokolov and S. A. Adonin, *Polyhedron*, 2021, **194**, 114895.

35 X. Li, R. Cao, D. Sun, D. Yuan, W. Bi, X. Li and Y. Wang, *J. Mol. Struct.*, 2004, **694**, 205.

36 T. Hökelek, E. Özbek, M. Sertçelik, Ç. Şahin Yenice and H. Necefoğlu, *Acta Crystallogr.*, 2017, **E73**, 1966.

37 H. Kwak, S. H. Lee, S. H. Kim, Y. M. Lee, B. K. Park, E. Y. Lee, Y. J. Lee, C. Kim, S.-J. Kim and Y. Kim, *Polyhedron*, 2008, **27**, 3484.

38 J.-H. Cai, Y.-H. Xu and S. W. Ng, *Acta Crystallogr.*, 2007, **E63**, m2940.

39 J. Wang, D. Ma, W. Liao, S. Li, M. Huang, H. Liu, Y. Wang, R. Xie and J. Xu, *CrystEngComm*, 2017, **19**, 5244.

40 D. A. Valyaev, M. A. Uvarova, A. A. Grineva, V. César, S. N. Nefedov and N. Lugan, *Dalton Trans.*, 2016, **45**, 11953.

41 A. Karmakar, R. J. Sarma and J. B. Baruah, *Inorg. Chem. Commun.*, 2006, **9**, 1169.

42 K. F. Konidaris, M. Kaplanis, C. P. Raptopoulou, S. P. Perlepes, E. Manessi-Zoupa and E. Katsoulakou, *Polyhedron*, 2009, **28**, 3243.

43 C.-H. Li, W. Li, H.-X. Hu and B.-N. Hu, *Chin. J. Struct. Chem*., 2015, **34**, 1405.

44 R. F. W. Bader, *Chem. Rev.*, 1991, **91**, 893.

45 A. A. Eliseeva, D. M. Ivanov, A. S. Novikov, A. V. Rozhkov, I. V. Kornyakov, A. Y. Dubovtsev and V. Y. Kukushkin, *Dalton Trans.*, 2020, **49**, 356.

46 A. A. Eliseeva, D. M. Ivanov, A. S. Novikov and V. Y. Kukushkin, *CrystEngComm*, 2019, **21**, 616.

47 V. V. Suslonov, N. S. Soldatova, D. M. Ivanov, B. Galmés, A. Frontera, G. Resnati, P. S. Postnikov, V. Y. Kukushkin and N. A. Bokach, *Cryst. Growth Des.*, 2021, **21**, 5360.

48 I. S. Aliyarova, D. M. Ivanov, N. S. Soldatova, A. S. Novikov, P. S. Postnikov, M. S. Yusubov and V. Y. Kukushkin, *Cryst. Growth Des.*, 2021, **21**, 1136.

49 S. Alvarez, *Dalton Trans.*, 2013, **42**, 8617.

50 E. V. Bartashevich and V. G. Tsirelson, *Russ. Chem. Rev.*, 2014, **83**, 1181.

51 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498.

52 J. Contreras-García, E. R. Johnson, S. Keinan, R. Chaudret, J.-P. Piquemal, D. N. Beratan and W. Yang, *J. Chem. Theory Comput.*, 2011, **7**, 625.

53 C. Xu, L. Li, Y. Wang, Q. Guo, X. Wang, H. Hou and Y. Fan, *Cryst. Growth Des.*, 2011, **11**, 4667.

54 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3.

55 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3.

Received: 28th February 2022; Com. 22/6816