ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2018, Vol. 44, No. 3, pp. 207–213. © Pleiades Publishing, Ltd., 2018.

Synthesis, Characterization, and Properties of a 1D Zinc(II) Complex from Substituted Imidazole Dicarboxylate[1]

X. S. Lin and Y. L. Sang*

College of Chemistry and Chemical Engineering, Chifeng University,
Chifeng, Neimenggu, 024000 P.R. China
**e-mail: sangyali0814@126.com*

Received June 27, 2017

Abstract—A one-dimensional zinc(II) polymer, $\{[Zn_2((p\text{-}FPhHIDC)(p\text{-}FPhH_2IDC)_2)(Phen)_2] \cdot H_2O\}_n$ (**I**) (p-FPhH_3IDC = 2-(p-fluorophenyl)-1H-imidazole-4,5-dicarboxylicacid (Phen = 1,10-phenanthroline), has been solvothermally synthesized and structurally characterized by single-crystal X-ray diffraction (CIF file CCDC no. 1063532), elemental analyses, and IR spectra. In polymer **I**, these 1D wave chains were joined through the π–π interactions and intermolecular hydrogen bonds to give a 2D architecture. The thermal properties of **I** have been determined in air.

Keywords: imidazole dicarboxylate, Zn(II), coordination polymer, crystal structure

DOI: 10.1134/S107032841803003X

INTRODUCTION

From 1990s to now, thousands of coordination polymers (CPs) built by metal ions and various organic ligands have been reported, which showed a variety of applications in the field of magnetism [1–3], luminescence [4–6], heterogeneous catalysts [7–9], drug delivery [10] and so on. However, the precise investigation of the structure and property of the CPs is still a challenge. We need to prepare more CPs with amusing crystalline structures to explore their promising properties.

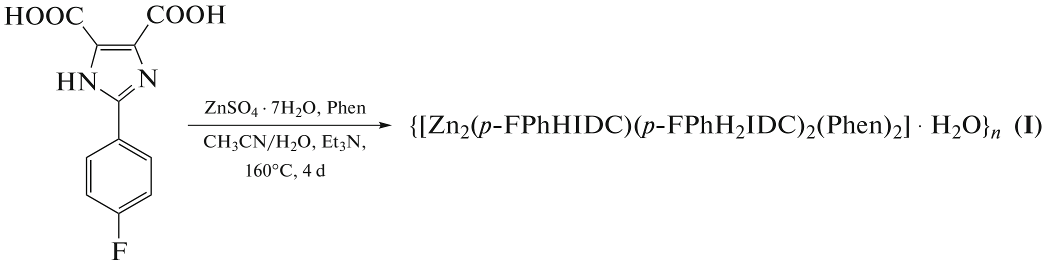
Obvious, fine design and choice of multifunctional organic ligands is a key to get diverse CPs [11]. At the same time, H-bonds also always play a crucial role in the construction of high dimensional solid crystalline structures [12]. Thus, the CPs with specific structures could be obtained under the synergistic interactions of coordination and H-bonds. For instance, a series of Zn-based CPs have been producing by varying organic ligands with different substituted groups (–OH [11–13], $-NH_2$ [14], –CHO [15] and –CN [16]).

More recently, people found that imidazole-based carboxylate ligands show strong coordination abilities and interesting coordination modes due to their several O and N donors. Consequently, several imidazole carboxylate-based CP sindicating one-dimensional (1D) chains [17, 18], two-dimensional (2D) grids [19], three-dimensional (3D) interpenetrated networks [20, 21] have been presented. Lots of groups have explored the strong coordination ability of the 2-position substituted on the imidazole ring of 1H-imidazole-4,5-dicarboxylate acid (H_3IDC). For example, 2-phenyl-1H-imidazole-4,5-dicarboxylic acid (PhH_3IDC) [22] has revealed outstanding coordination ability, and constructed some useful MOFs. Inspired by above interesting results, we hope to adopt a modified imidazole dicarboxylate ligand, 2-(p-fluorophenyl)-1H-imidazole-4,5-dicarboxylic acid (p-FPhH_3IDC), and synthesize more related CPs.

From the previous report [23], we know that p-FPhH_3IDC exhibit good advantages. In this study, the p-FPhH_3IDC ligand reacts with transition metal Zn(II) salt under solvothermal conditions. Fortunately, one novel coordination polymer, $\{[Zn_2((p\text{-}FPhHIDC)(p\text{-}FPhH_2IDC)_2)(Phen)_2] \cdot H_2O\}_n$ (**I**) (Phen = 1,10-phenanthroline), has been prepared and structurally characterized (Scheme 1). Here, we present the single-crystal X-ray diffraction, IR spectra, elemental analyses, and thermal properties of the complex **I** and describe coordination features of p-FPhH_3IDC ligand.

---

[1] The article is published in the original.



Scheme 1.

EXPERIMENTAL

Materials and methods. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The organic ligand *p*-FPhH_3IDC was prepared according to literature method [23, 24]. The C, H, and N microanalyses were carried out on a FLASH EA 1112 analyzer. IR spectra were recorded on a BRUKER TENSOR 27 spectrophotometer as KBr pellets in the 400–4000 cm^{-1} region. Thermogravimetric measurements were performed by heating the crystalline sample from 30 to 835°C at a rate of 10°C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer.

Synthesis of I. A mixture of $ZnSO_4 \cdot 7H_2O$ (33.8 mg, 0.1 mmol), *p*-FphH_3IDC (25.0 mg, 0.1 mmol), CH_3CN (3 mL), H_2O (4 mL) and Et_3N (0.014 mL, 0.1 mmol) was sealed in a 25 mL Teflon-lined stainless steel autoclave, heated at 150°C for four days, and then cooled to room temperature. Light yellow monoclinic crystals of **I** were isolated, washed with distilled water, and dried in air (68% yield based on Zn).

For $C_{57}H_{35}N_{10}O_{13}F_3Zn_2$

anal. calcd., %	C, 54.55	H, 2.79	N, 11.16
found, %	C, 54.42	H, 2.68	N, 11.08

IR (KBr; ν, cm^{-1}): 3480 m, 3049 w, 1672 m, 1563 s, 1527 m, 1449 s, 1269 m, 1220 s, 1005 w, 847 s, 862 m, 725 s.

X-ray crystallography. Measurements of compound **I** was made on a Bruker smart APEXII CCD diffractometer with a graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å). Single crystal of **I** was selected and mounted on a glass fiber. All data were collected at room temperature using the ω–2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied.

The structure was solved by direct methods and expanded using the Fourier technique. The non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included but not refined. The final cycle of full-matrix least squares refinement was based on 9035 observed reflections and 613 variable parameters. All calculations were performed using the SHELX-97 crystallographic software package [25].

Crystal data and experimental details is contained in Table 1. The selected bond lengths and angles, and H-bond parameters are listed in Tables 2 and 3, respectively.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1063532; deposit@ccdc.cam.ac.uk or https://www.ccdc.cam.ac.uk/deposit).

RESULTS AND DISCUSSION

A single-crystal X-ray diffraction study shows that compound **I** is a 1D structure. An appropriate drawing of the complex structure with atom labeling scheme is shown in Fig. 1a.

The asymmetric unit of **I** consists of two central Zn(1) and Zn(2) atoms, one *p*-FPhHIDC^{2-} and two *p*-FPhH_2IDC$^-$ anions, two Phen molecules and a free water molecule. The geometry around the Zn(II) center is best portrayed as a distorted [ZnO_2N_4] octahedral environment. Taking Zn(1) for instance, which includes two imidazole nitrogen (N(5) and N(9)), carboxylate oxygen atom O(3) from *p*-FPhHIDC^{2-} anion and O(10) of *p*-FPhH_2IDC$^-$, and N(1) and N(2) from the coordinated Phen (Fig. 1a). The Zn–O distances span from 2.137(3) to 2.147(3) Å, while Zn–N bond lengths are in the range of 2.005(3)–2.220(3) Å. The bond angles around the central Zn^{2+} ion vary from 75.69(11)° to 162.91(12)°.

Each *p*-FPhHIDC^{2-} ligand adopts the same coordination mode, namely, μ_2-*k*O, N : *k*O', *k*N' (Fig. 2). It should be point that the *p*-FPhHIDC^{2-} units and water molecule participate in the formation of hydrogen bonds, which are an integral part of the crystal structure. As we can see, in a 1D spiral chain, a imidazole dicarboxylate ligand bridges two metal atoms, and the dihedral angles between the imidazole and the phenyl planes are 58.81(12)° and 86.21(11)°, indicating the serious twist. Thus, the different degree of deformation of *p*-FPhHIDC^{2-} units make Zn(1) and

Table 1. Crystallographic data and structure refinement information for compound **I**

Parameter	Value
Temperature, K	296(2)
Fw	91.32
Crystal system	Monoclinic
Crystal size, mm	0.21 × 0.20 × 0.19
Space group	$P2_1/n$
a, Å	10.205(2)
b, Å	18.091(4)
c, Å	22.075(5)
β, deg	103.202(3)
V, Å^3	3967.6(15)
ρ_{calcd}, mg m^{-3}	1.682
Z	4
μ, mm^{-1}	1.292
Reflections collected	23331
R_{int}	0.0506
Data with $I > 2\sigma(I)$/restraints/parameters	9035/4/613
GOOF on F^2	0.990
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0503$, $wR_2 = 0.1316$
R indices (all data)	$R_1 = 0.0944$, $wR_2 = 0.1573$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$, e Å^{-3}	0.818 and –0.536

Zn(2) have different coordination environments (Fig. 1a). All the phenyl rings of the same position are parallel to each other. The distances between two neighboring phenyl rings are 3.801 and 5.752 Å, respectively. Also, the planes of two neighboring Phen molecules of the same position are parallel; the related plane distances are 6.371 and 6.810 Å, respectively. All these π···π stacking interactions of the phenyl rings and Phen vary in intensity. In addition, there are two types of hydrogen bonds in complex **I**. One is the intramolecular H-bonds consisting of O(4)–H(4)···O(6). The other is intermolecular H-bonds, O(14)–H(51)···O(5) and O(14)–H(53)···O(10), which link the adjacent chains to build up a 2D structure (Fig. 1b).

The strong and broad absorption bands around 3400–3500 cm^{-1} should be ascribed to the stretching vibrations of O–H and N–H, suggesting the presence of free water molecule and imidazole ring, respectively. The asymmetric and symmetric stretching vibrations of carboxyl group appeared at 1672 and

Table 2. Selected bond distances (Å) and angles (deg) for complex **I***

Bond	*d*, Å	Bond	*d*, Å
Zn(1)–N(9)	2.005(3)	Zn(1)–N(5)	2.036(3)
Zn(1)–N(1)	2.170(3)	Zn(1)–N(2)	2.170(3)
Zn(1)–O(3)	2.417(3)	Zn(1)–O(10)	2.417(3)
Zn(2)–N(11)$^{\#1}$	2.066(3)	Zn(2)–N(4)	2.126(3)
Zn(2)–O(5)	2.137(3)	Zn(2)–N(7)	2.147(3)
Zn(2)–N(6)	2.220(3)	Zn(2)–O(13)$^{\#1}$	2.255(3)
Angle	ω, deg	Angle	ω, deg
N(9)Zn(1)N(5)	142.12(12)	N(9)Zn(1)N(2)	105.36(11)
N(5)Zn(1)N(1)	108.58(12)	N(1)Zn(1)N(2)	76.67(12)
N(5)Zn(1)N(2)	102.71(11)	N(5)Zn(1)O(3)	75.69(11)
N(9)Zn(1)O(3)	82.65(11)	N(2)Zn(1)O(3)	83.65(11)
N(1)Zn(1)O(3)	160.32(11)	N(5)Zn(1)O(10)	104.32(12)
N(9)Zn(1)O(10)	75.84(11)	N(2)Zn(1)O(10)	162.91(12)
N(1)Zn(1)O(10)	86.39(11)	N(11)$^{\#1}$Zn(2)N(4)	104.32(12)
O(3)Zn(1)O(10)	113.27(11)	N(4)Zn(2)O(5)	79.49(11)
N(11)$^{\#1}$Zn(2)O(5)	161.31(11)	N(9)Zn(1)N(1)	102.29(12)
N(11)$^{\#1}$Zn(2)N(7)	89.45(12)	N(4)Zn(2)N(7)	162.01(12)
O(5)Zn(2)N(7)	91.19(11)	N(11)$^{\#1}$Zn(2)N(6)	104.25(11)
N(4)Zn(2)N(6)	88.87(12)	O(5)Zn(2)N(6)	94.04(11)
N(7)Zn(2)N(6)	76.38(13)	N(11)$^{\#1}$Zn(2)O(13)$^{\#1}$	77.52(11)
N(4)Zn(2)O(13)$^{\#1}$	89.55(11)	O(5)Zn(2)O(13)$^{\#1}$	84.28(10)
N(7)Zn(2)O(13)$^{\#1}$	104.92(12)	N(6)Zn(2)O(13)$^{\#1}$	177.88(10)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x + 1/2, y + 1/2, -z + 1/2$.

Table 3. Hydrogen bond distances (Å) and angles (deg) for complex **I**

D–H···A	Distance, Å		Angle DHA, deg
	H···A	D···A	
O(4)–H(4)···O(6)	1.68	2.491(1)	172
O(14)–H(51)···O(3)	2.06	2.927(3)	175
O(14)–H(53)···O(12)	2.34	3.136(2)	154
O(14)–H(53)···O(9)	2.41	3.099(2)	138

1563 cm^{-1}, which indicates the existence of free and coordinated carboxyl groups. The bands in the range of 600–800 cm^{-1} correspond to the benzene ring. In conclusion, IR spectrum is consistent with the results of the X-ray diffraction analysis.

As is indicated in Fig. 3, there are three-step of mass loss in **I**. The first weight loss from 30.0 to 257.5°C, which is corresponding to the weight loss of the free water molecule (obsd. 1.99%, calcd. 1.73%). Then, the ancillary Phen ligands begin to collapse with weight loss is 33.59% (calcd. 134.72%) from 257.5 to 457.5°C. It keeps losing weight from 457.5 to 685.0°C, which corresponds to the removal of the imidazole dicarboxylate ligands (obsd. 47.57%, calcd. 147.94%). Finally, a plateau region is observed from 685.0 to 835.0°C. The remaining weight residue is ZnO (obsd. 16.85%, calcd. 115.61%).

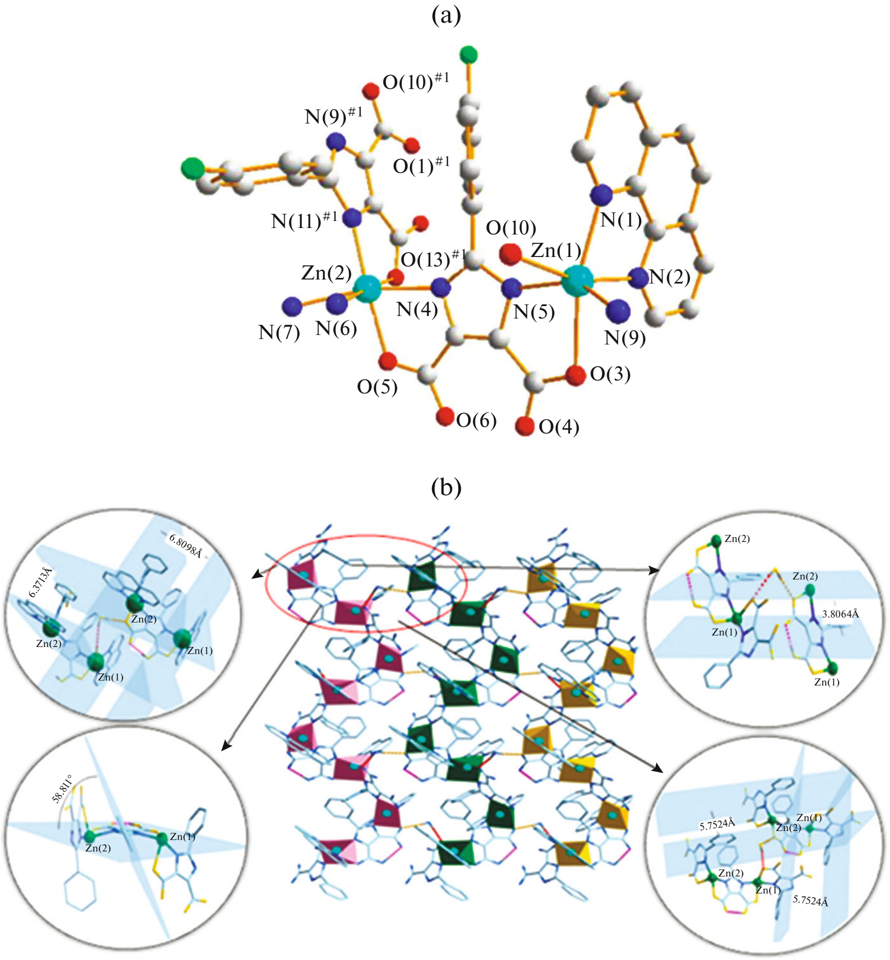


Fig. 1. Coordination environments of the Zn(II) atoms in **I** (a); a 2D plane structure (b; deleting sectional hydrogen).

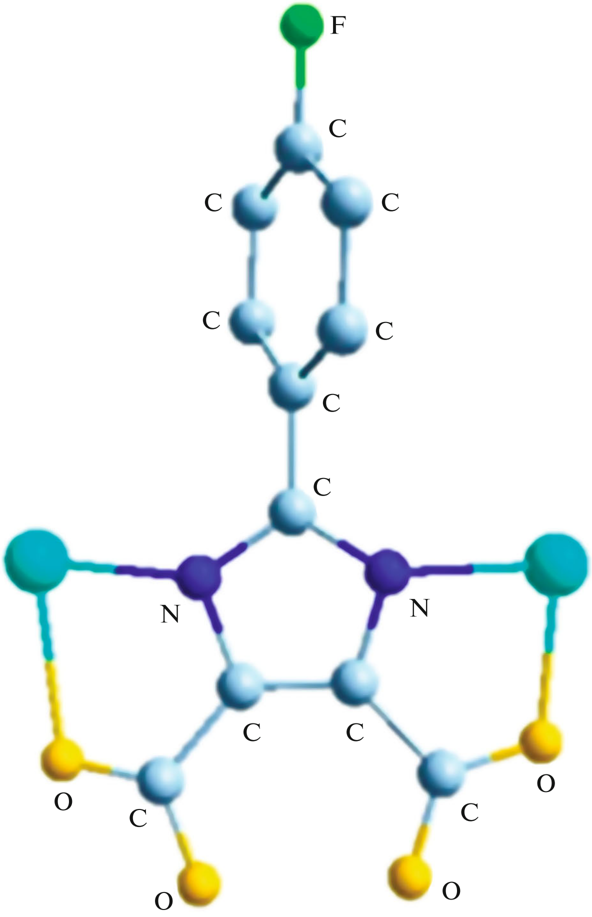


Fig. 2. Coordination mode of imidazole dicarboxylate ligand in **I**.

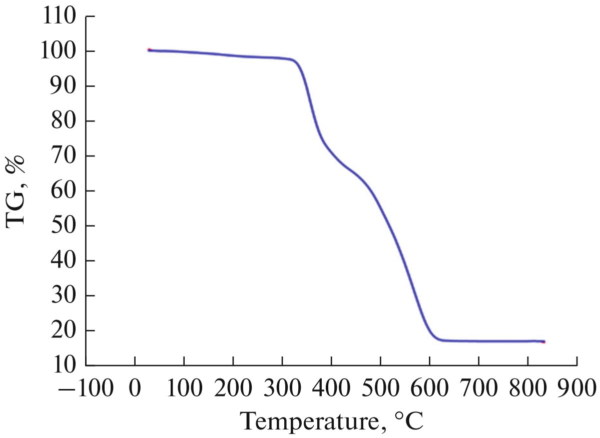


Fig. 3. TG analysis curve of **I**.

In summary, a transition-metal-organic architecture has been successfully prepared by using the designed p-FPhH$_3$IDC ligand. The crystal structure has been characterized by single-crystal X-ray diffraction, IR spectra, elemental analyses and thermal analyses. The architecture reveals the strong coordination ability of the p-FPhH$_3$IDC ligand.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support by the Research Program of Science and Technology at Universities of Inner Mongolia Autonomous Region (nos. NJZY238 and NJZY239), Inner Mongolia Key Laboratory of Photoelectric Functional Materials, Chifeng University Key Laboratory of Photoelectric Functional Materials, and Chifeng University Science and Research Creative Team.

REFERENCES

1. Bhattacharjee, S., Yang, D.A., and Ahn, W.S., *Chem. Commun.*, 2011, vol. 47, p. 3637.
2. Wang, J., Xu, H., Qian, X., et al., *Chem. Asian J.*, 2015, vol. 10, p. 1276.
3. Gao, J., Miao, J., Li, P.Z., et al., *Chem. Commun.*, 2014, vol. 50, p. 3786.

4. Gao, J., Ye, K., Yang, L., et al., *Inorg. Chem.*, 2014, vol. 53, p. 691.
5. McNamara, N.D., Neumann, G.T., Masko, E.T., et al., *J. Catal.*, 2013, vol. 305, p. 217.
6. McNamara, N.D. and Hicks, J.C., *ACS Appl. Mater. Interfaces*, 2015, vol. 7, p. 5338.
7. Rosi, N.L., Eckert, J., Eddaoudi, M., et al., *Science*, 2003, vol. 300, p. 1127.
8. Kim, J., Oliver, A.G., Neumann, G.T., and Hicks, J.C., *Eur. J. Inorg. Chem.*, 2015, vol. 2015, p. 3011.
9. Tan, J.-C. and Civalleri, B., *CrystEngComm*, 2015, vol. 17, p. 197.
10. Kwon, H.T. and Jeong, H.K., *Chem. Commun.*, 2013, vol. 49, p. 3854.
11. Adarsh, N., Kumar, D.K., and Dastidar, P., *CrystEngComm*, 2009, vol. 11, p. 796.
12. Desiraju, G.R., *Angew. Chem. Int. Ed.*, 1995, vol. 34, p. 231.
13. Kim, J., Kim, D.O., Kim, D.W., et al., *Inorg. Chim. Acta*, 2012, vol. 390, p. 22.
14. Eddaoudi, M., Kim, J., Rosi, N., et al., *Science*, 2002, vol. 295, p. 469.
15. Burrows, A.D., Frost, C.G., Mahon, M.F., and Richardson, C., *Angew. Chem. Int. Ed.*, 2008, vol. 47, p. 8482.
16. Furukawa, H., Kim, J., Ockwig, N.W., et al., *J. Am. Chem. Soc.*, 2008, vol. 130, p. 11650.
17. Bai, Y.L., Tao, J., Huang, R.B., and Zheng, L.S., *Angew. Chem. Int. Ed.*, 2008, vol. 47, p. 5344.
18. Ma, S., Yuan, D., Wang, X.S., and Zhou, H.C., *Inorg. Chem.*, 2009, vol. 48, p. 2072.
19. Wang, Z.X., Wu, Q.F., Liu, H.J., et al., *CrystEngComm*, 2010, vol. 12, p. 1139.
20. Liu, G.Z., Wang, J.G., and Wang, L.Y., *CrystEngComm*, 2012, vol. 14, p. 951.
21. Zhang, X.M., Hao, Z.M., Zhang, W.X., and Chen, X.M., *Angew. Chem. Int. Ed.*, 2007, vol. 46, p. 3456.
22. Wang, W.Y., Niu, X.L., Gao, Y.C., et al., *Cryst. Growth Des.*, 2010, vol. 10, p. 4050.
23. Yao, M.J., Ren, X., Yue, Z.F., and Li, G., *Russ J. Coord. Chem.*, 2015, vol. 41, p. 524.
24. Lebedev, A.V., Lebedeva, A.B., Sheludyakov, et al., *Russ. J. Gen. Chem.*, 2007, vol. 77, p. 855.
25. Pachfule, P., Das, R., Poddar, P., and Banerjee, R., *Inorg. Chem.*, 2011, vol. 50, p. 3855.