ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 12, pp. 856–861. © Pleiades Publishing, Ltd., 2023.

Reactivity of Half-Sandwich 16e Carborane Complex $Me_4CpCo[S_2C_2B_{10}H_{10}]$ with Phosphorous Compounds

Y. Huang[a], **Q. Xiao**[a], **G. R. Xu**[a], **H. D. Ye**[a, *], **H. N. Peng**[a, **], **and X. L. Zhang**[a]

[a] *School of Chemistry and Environmental Science, Jiangxi Provincial Research of Targeting Pharmaceutical Engineering Technology, Shangrao Normal University, Jiangxi, 334001 P.R. China*

**e-mail: yehongde@163.com*

***e-mail: huananpeng@126.com*

Received March 31, 2023; revised April 12, 2023; accepted May 4, 2023

Abstract—Treatment of *o*-carborane, *n*-butyllithium, sulfur and $Me_4CpCo(CO)I_2$ under argon leads to half-sandwich 16e carborane complex $Me_4CpCo[S_2C_2B_{10}H_{10}]$. $Me_4CpCo[S_2C_2B_{10}H_{10}]$ reacts with PPh_2Me, $PPhMe_2$, PMe_3 to afford addition products $Me_4CpCo[S_2C_2B_{10}H_{10}](PPh_2Me)$ (**I**), $Me_4CpCo[S_2C_2B_{10}H_{10}](PPhMe_2)$ (**II**), $Me_4CpCo[S_2C_2B_{10}H_{10}](PMe_3)$ (**III**), respectively. **I**, **II** and **III** have been characterized by IR, NMR, elemental analysis, mass spectrum. **I** and **III** have also been characterized by single-crystal X-ray diffraction analysis (CCDC nos. 2245287 (**I**) and 2245288 (**III**)). The UV and fluorescent spectra properties of the compounds **I**, **II** and **III** have been tested. The UV spectra results of complexes **I**, **II** and **III** in acetonitrile solution show that the bands are located at 412, 399 and 401 nm, respectively. The fluorescence spectra result of the complexes **I**, **II** and **III** exhibit maximum emission peaks at about 405 nm.

Keywords: *o*-carborane, half-sandwich, characterization, phosphorous compound

DOI: 10.1134/S107032842360050X

INTRODUCTION

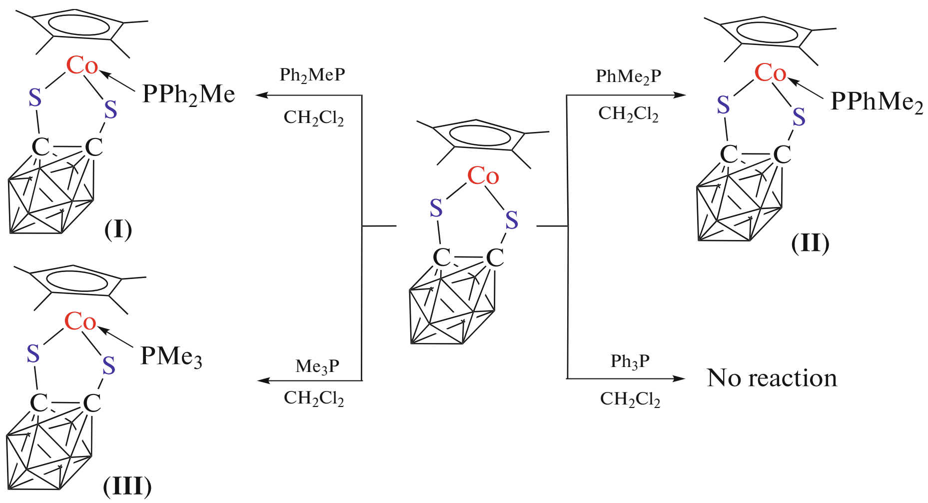
The icosahedral *closo*-carboranes ($C_2B_{10}H_{12}$) can be divided into three isomers according to the relative position of the two carbon atoms in the molecules: 1,2-$C_2B_{10}H_{12}$, 1,7-$C_2B_{10}H_{12}$, and 1,12-$C_2B_{10}H_{12}$ (i.e., *o*-carborane, *m*-carborane, *p*-carborane). In recent years, these icosahedral *closo*-carboranes have been extensively studied due to their unique 3D pseudoaromatic geometry and push-pull electron properties [1–6], and the photophysical properties of carboral-containing structural unit materials have attracted increasing research interest [7]. Carborane structural units are introduced into luminescent materials to improve their luminescence properties [8]. Carboranes are used as an effective structural material in the organic and polymer fields in order to obtain excellent luminescent and electronic materials [9], and carborane structural units are introduced into fluorescent organic systems [10], polymers [11] and metal complexes [12]. Experimental results show that carboranes play a unique role in coordinating the physical properties of light. However, the role of the carborane cage itself still needs further study in terms of the photophysical properties of the carborane-containing structural unit materials, especially for *o*-carborane derivatives, which have a unique C—C bond (bonding range of 0.162–0.215 nm) [13] and are generally light-extinguishable [14].

In recent years, the ultraviolet and fluorescence properties of cobalt-containing metal ion complexes [15, 16] have been extensively studied. But to the best of our knowledge, the fluorescence and ultraviolet properties of carborane derivatives containing cobalt ions have not yet been tested. In our recent work, we synthesized some carborane derivatives containing cobalt metal and tested fluorescence and UV properties of these carborane derivatives [17]. As a continuation of our previous work, we report the reactions of the half-sandwich 16e carborane compound $Me_4CpCo[S_2C_2B_{10}H_{10}]$ with PPh_2Me, $PPhMe_2$, PMe_3 and test the fluorescence and UV properties of the synthesized products.

EXPERIMENTAL

Materials and methods. All experiments were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were dried by refluxing over sodium (petroleum ether, ether, and THF) or calcium hydride (dichloromethane) under nitrogen and then distilled prior to use. *n*-Butyllithium (2.0 M in cyclohexane, Aldrich), *o*-carborane (Acros), diphenylmethylphosphine, phenyldimethylphosphine, trimethylphosphine, triphenylphosphine (Aladdin) and other chemicals were used as commercial products without further purification. Me_4CpCo-

$[S_2C_2B_{10}H_{10}]$ was prepared according to literature [18]. Elemental analysis was performed in an elementar vario EL III elemental analyzer. NMR data were recorded on a Bruker DRX-500 spectrometer. ^1H NMR and ^{13}C NMR spectra were reported in ppm with respect to $CHCl_3/CDCl_3$ (δ ^1H = 7.26, δ ^{13}C = 77.0) and ^{11}B NMR spectra were reported in ppm with respect to external $Et_2O{-}BF_3$ (δ ^{11}B = 0). The IR spectra were recorded on a Bruker Vector 22 spectrophotometer with KBr pellets in the 4000–400 cm^{-1} region. The mass spectra were recorded on Thermo Fisher Scientific for ESI-MS.



Scheme 1. Reactions of $Me_4CpCo[S_2C_2B_{10}H_{10}]$ with phosphorous compounds [17].

Synthesis of complexes I, II and III. Diphenylmethylphosphine (60.1 mg, 0.3 mmol) was added to a solution of $Me_4CpCo[S_2C_2B_{10}H_{10}]$ (115.9 mg, 0.3 mmol) in dry CH_2Cl_2 (20 mL). The resulting mixture was stirred for 10 h at ambient temperature. After removal of the solvent, the residue was chromatographed on silica gel. Elution with petroleum ether–CH_2Cl_2 (1 : 2 v/v) gave pure compound **I** (165.4 mg, 94% yield) as black solid. Complexes **II** and **III** were synthesized by the similar methods when using $PPhMe_2$, PMe_3 instead of PPh_2Me in 95% yield for **II** and 93% yield for **III**, respectively. Suitable single crystals of **I** and **III** were obtained by slow diffusion of petroleum ether into their CH_2Cl_2 solutions, respectively.

For $C_{24}H_{36}B_{10}S_2PCo$ (**I**)

Anal. calcd., %	C, 49.13	H, 6.18
Found, %	C, 49.09	H, 6.20

ESI-MS (positive mode, $CH_2Cl_2{-}CH_3OH$ = 5 : 1): *m/z* = 625.48 $[C_{24}H_{36}B_{10}S_2PCoK]^+$. ^1H NMR ($CDCl_3$; δ, ppm): 7.67–7.43 (m., 10H, Ph), 4.05 (d., 1H, *J* = 6.0 Hz, $Me_4Cp{-}C\mathit{H}$), 2.01 (d., 3H, *J* = 10.9 Hz, $C\mathit{H}_3$), 1.63 (d., 6H, *J* = 3.1 Hz, $C\mathit{H}_3$), 0.81 (s., 6H, $C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$; δ, ppm): 133.36; 132.32; 130.85; 128.61; 111.26; 94.59; 88.07; 84.14; 10.36; 10.22. $^{11}B\{^1H\}$ NMR ($CDCl_3$; δ, ppm): –1.42, –4.63, –7.78 (3 : 4 : 3). IR (ν, cm^{-1}): 2575 (B–H).

For $C_{19}H_{34}B_{10}S_2PCo$ (**II**)

Anal. calcd., %	C, 43.50	H, 6.53
Found, %	C, 43.48	H, 6.50

ESI-MS (positive mode, CH_2Cl_2/CH_3OH = 5 : 1): *m/z* = 563.52 $[C_{19}H_{34}B_{10}S_2PCoK]^+$. ^1H NMR ($CDCl_3$; δ, ppm): 7.62–7.44 (m., 5H, Ph), 3.92 (d., 1H, *J* = 6.8 Hz, $Me_4Cp{-}C\mathit{H}$), 1.83 (d., 6H, *J* = 11.12 Hz, $C\mathit{H}_3$), 1.65 (d., 6H, *J* = 3.2 Hz, $C\mathit{H}_3$), 0.82 (d., 6H, *J* = 1.5 Hz, $C\mathit{H}_3$). ^{13}C NMR ($CDCl_3$; δ, ppm): 137.03; 130.55; 129.02; 128.88; 111.09; 94.88; 86.57; 15.72; 10.11; 9.92. $^{11}B\{^1H\}$ NMR ($CDCl_3$; δ, ppm): –1.79, –5.03, –7.35 (3 : 3 : 4). IR (ν, cm^{-1}): 2577 (B–H).

For $C_{14}H_{32}B_{10}S_2PCo$ (**III**)

Anal. calcd., %	C, 36.35	H, 6.97
Found, %	C, 36.39	H, 7.01

ESI-MS (negitive mode, CH_3OH): *m/z* = 571.34 $[C_{14}H_{32}B_{10}S_2PCo$ + DMSO + $CH_3O]^-$. ^1H NMR ($CDCl_3$; δ, ppm): 4.23 (d., 1H, *J* = 6.7 Hz, $MeCp{-}C\mathit{H}$) , 1.73 (d., 6H, *J* = 3.2 Hz, $C\mathit{H}_3$), 1.56 (d., 9H, *J* = 11.0 Hz, $C\mathit{H}_3$), 1.33 (d., 6H, *J* = 1.6 Hz, $C\mathit{H}_3$). ^{13}C

Table 1. Crystallographic data and structural refinement details of complexes **I** and **III**

Parameter	Value	
	I	**III**
Crystal size, mm	0.20 × 0.18 × 0.15	0.20 × 0.18 × 0.15
Formula weight	586.65	462.52
Temperature, K	223(2)	298(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C1c1$
a, Å	12.9903(4)	11.6163(5)
b, Å	15.9926(4)	16.3835(7)
c, Å	14.5945(4)	25.4763(9)
α, deg	90.00	90.00
β, deg	104.952(2)	100.090(4)
γ, deg	90.00	90.00
V, Å^3	2929.33(14)	4773.5(3)
Z	4	4
ρ_{calcd}, g cm^{-3}	1.330	1.287
μ, mm^{-1}	4.428	0.960
F(000)	1216	1920
θ Range, deg	3.636–53.932	3.482–29.323
Reflections collected	13132	34733
Independent reflections (R_{int})	5074 (0.0421)	11087 (0.0289)
Reflections observed ($I > 2\sigma(I)$)	4510	9951
Data/restrains/parameters	5074/0/364	11087/2/520
GOOF	1.036	1.047
R_1, wR_2 ($I > 2\sigma(I)$)	0.0325, 0.0834	0.0333, 0.0745
R_1, wR_2 (all data)	0.0382, 0.0874	0.0398, 0.0783
Largest difference peak/hole, e Å^{-3}	0.388/–0.389	0.351/–0.224

NMR ($CDCl_3$; δ, ppm): 111.62; 94.86; 85.85; 84.96; 18.15; 17.82; 11.05; 9.99. $^{11}B\{^1H\}$ NMR ($CDCl_3$; δ, ppm): –1.85, –5.86, –8.59 (2 : 5 : 3). IR (ν, cm^{-1}): 2573(B–H).

X-ray crystallographic studies. Suitable single crystals of **I** and **III** were selected and mounted in air onto thin glass fibers. X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer at 291(2) K using MoK_α radiation (λ = 0.71073 Å) by multi-scan mode. The SAINT program was used for integration of the diffraction profiles. The structures were solved by direct methods using the SHELXS-97 [19] program package and refined against F^2 by full-matrix least-squares with SHELXL-97 [20]. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on carbon were set in calculated positions and refined as riding. The crystallographic data are summarized in Table 1 and selected bond lengths and angles are listed in Table 2 containing the supplementary crystallographic data for this article.

Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre (nos. 2245287 (**I**) and 2245288 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The reactivity of 16e half-sandwich carborane compounds has been investigated extensively [21]. Owing to their unsaturated metal center, two reactive M–E (E = S, Se) bonds and potentially reactive carborane cage with activated B–H bonds, these sterically congested, mononuclear coordination compounds can be stored conveniently and be used for further transformation in a controlled way under various conditions. Previous studies have shown that the reactivity of 16e half-sandwich carborane compounds, product strucures and formation mechanisms are

Table 2. Selected bond lengths (Å) and bond angles (deg) for **I** and **III**

Bond	*d*, Å	Angle	ω, deg
		I	
C(1)–C(2)	1.658(3)	S(1)Co(1)S(2)	92.70(2)
C(1)–S(1)	1.789(2)	C(1)C(2)S(2)	116.95(13)
C(2)–S(2)	1.783(2)	C(2)C(1)S(1)	116.27(13)
S(1)–Co(1)	2.2602(6)	C(1)S(1)Co(1)	104.09(7)
S(2)–Co(1)	2.2440(6)	C(2)S(2)Co(1)	103.96(7)
Co(1)–P(1)	2.2602(6)	S(1)Co(1)P(1)	89.42(2)
P(1)–C(12)	1.822(2)	S(2)Co(1)P(1)	93.29(2)
P(1)–C(18)	1.829(2)	Co(1)P(1)C(12)	111.22(7)
P(1)–C(24)	1.818(2)	Co(1)P(1)C(18)	119.08(7)
		Co(1)P(1)C(24)	118.49(8)
		III	
C(1)–C(2)	1.657(5)	S(1)Co(1)S(2)	92.70(4)
C(1)–S(1)	1.787(4)	C(1)C(2)S(2)	117.1(2)
C(2)–S(2)	1.787(4)	C(2)C(1)S(1)	116.0(2)
S(1)–Co(1)	2.2527(11)	C(1)S(1)Co(1)	103.93(12)
S(2)–Co(1)	2.2422(11)	C(2)S(2)Co(1)	103.68(12)
Co(1)–P(1)	2.1881(13)	S(1)Co(1)P(1)	92.12(5)
P(1)–C(12)	1.796(6)	S(2)Co(1)P(1)	90.24(5)
P(1)–C(13)	1.828(6)	Co(1)P(1)C(12)	114.3(3)
P(1)–C(14)	1.819(5)	Co(1)P(1)C(13)	113.8(2)
		Co(1)P(1)C(14)	118.73(16)

dependent on the metal center, the chalcogen element, the ancillary ligand on metal of 16e half-sandwich carborane compounds. For example, triphenylphosphine can react with MeCpCo[$S_2C_2B_{10}H_{10}$] but reacts neither with Cp*Co[$S_2C_2B_{10}H_{10}$] nor with Cp*Co[$Se_2C_2B_{10}H_{10}$] [22]. The root cause is that the size of the ancillary ligand Cp* is larger than that of MeCp, which hinder the reactions of triphenylphosphine with Cp*Co[$S_2C_2B_{10}H_{10}$] and Cp*Co-[$Se_2C_2B_{10}H_{10}$]. Our previous work shows that the reactivity of Cp*Co[$S_2C_2B_{10}H_{10}$] is similar to that of Me_4CpCo[$S_2C_2B_{10}H_{10}$] while the reactivity of CpCo[$S_2C_2B_{10}H_{10}$] is similar to that of MeCpCo-[$S_2C_2B_{10}H_{10}$]. Herein we conduct the reactions of Me_4CpCo[$S_2C_2B_{10}H_{10}$] with PPh_2Me, $PPhMe_2$, PMe_3 and triphenylphosphine. As expected, Me_4CpCo[$S_2C_2B_{10}H_{10}$] reactions with PPh_2Me, $PPhMe_2$, PMe_3 to get stable 1 : 1 adduct products **I**, **II** and **III**, respectively, but can't react with triphenylphosphine. **I**, **II** and **III** have been characterized by nuclear magnetic resonance, mass spectrometry and infrared. **I** and **III** have also been characterized by single crystal X-ray diffraction. We take **I** as an example to discuss their crystal structures. The solid-state structure of **I** (Fig. 1a) shows that it is an addition structure. PPh_2Me reacts with Me_4CpCo[$S_2C_2B_{10}H_{10}$] by coordinate-covalent bond to form **I**. The coordinate-covalent bond P–Co distance is 2.2602(6) Å and falls in the normal coordinative bond P→Co bond range. The five-membered ring S(1)C(1)-C(2)S(2)Co(1) in **I** is no longer planar because of the insertion of PPh_2Me. The dihedral angle between the planes S(1)Co(1)S(2) and S(1)C(1)C(2)S(2) at the S(1)···S(2) vector is 156.7°. The spectroscopic and analytical data of **I** are consistent with its solid-state structure. In the ^{1}H NMR data, the multiple peaks at 7.67–7.43 ppm are assigned to two Ph rings, the doulblet peaks at 4.057 and 4.042 ppm are signals of the CH group in Me_4Cp ring, while three peaks at 2.01, 1.63 and 0.81 ppm are the resonance of five CH_3 groups in **I**.

The UV spectra of the compounds **I**, **II** and **III** in acetonitrile (1×10^{-5} mol/L) are shown in Fig. 2, and the fluorescence spectrum are shown in Fig. 3. According to the UV absorption spectra, the absorption peaks of **I**, **II** and **III** in acetonitrile are located at 412, 399 and 401 nm, respectively. The absorption peaks corresponds to the electronic transition of the charge transfer within the molecules [23]. The fluorescence spectra show that the maximum emission

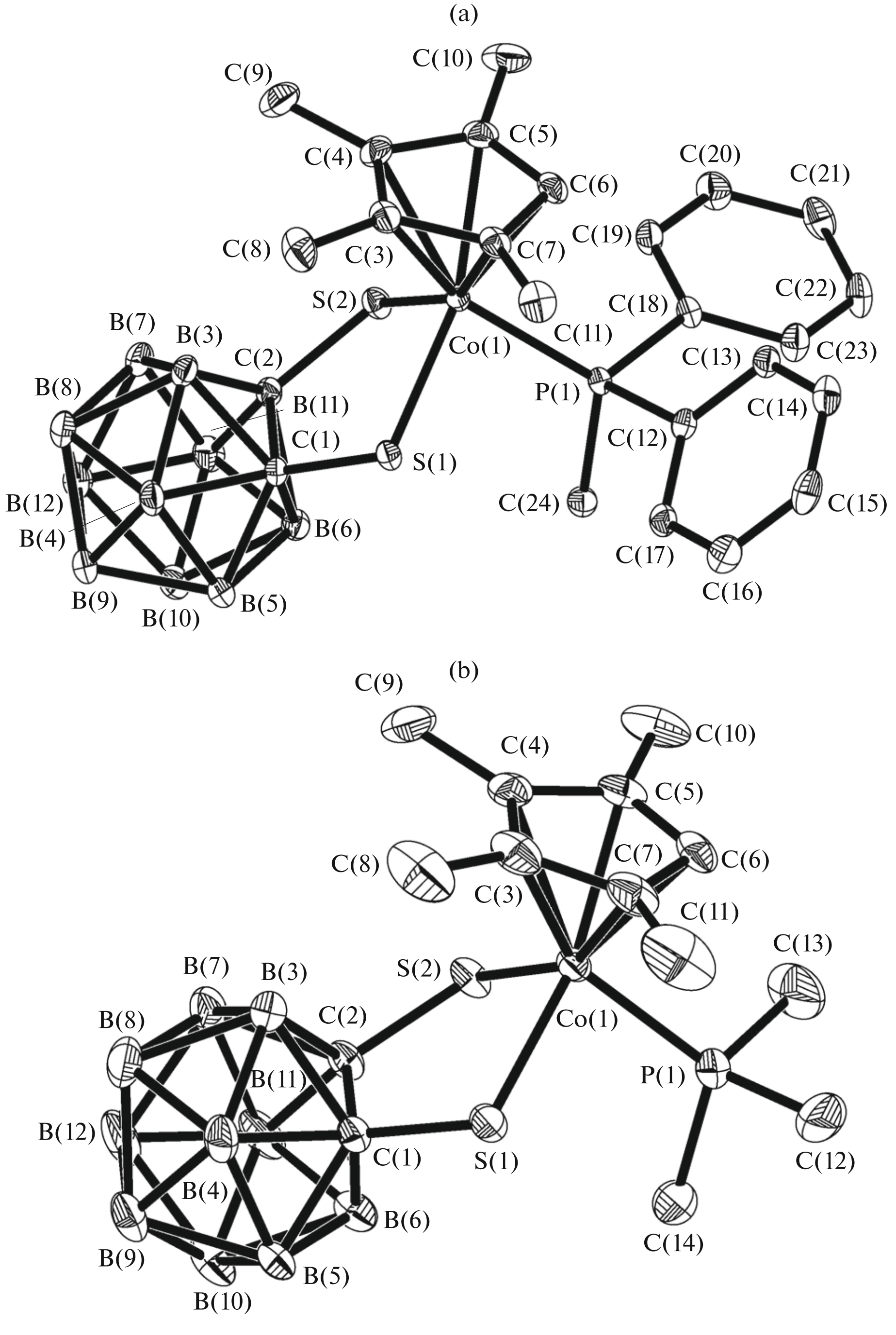


Fig. 1. Molecular structures of **I** (a) and **III** (b).

wavelength of compounds **I**, **II** and **III** in acetonitrile is about 405 nm.

CONCLUSIONS

The half-sandwich carborane 16e compound $Me_4CpCo[S_2C_2B_{10}H_{10}]$ reactions with PPh_2Me, $PPhMe_2$, PMe_3 to give stable 1 : 1 adduct products **I**, **II** and **III**, respectively, but cannot react with triphenylphosphine. Our previous studies have shown that triphenylphosphine can react with MeCpCo-$[S_2C_2B_{10}H_{10}]$ but cannot react with $Cp^*Co[S_2C_2B_{10}H_{10}]$. The root cause is that the size of the ancillary ligand Me_4Cp is larger than that of MeCp, which hinder the reactions of triphenylphosphine with $Me_4CpCo[S_2C_2B_{10}H_{10}]$. The reactivity of $Me_4CpCo[S_2C_2B_{10}H_{10}]$ is similar to that of $Cp^*Co[S_2C_2B_{10}H_{10}]$. The structures of **I**, **II** and **III** have been characterized by IR, NMR, elemental anal-

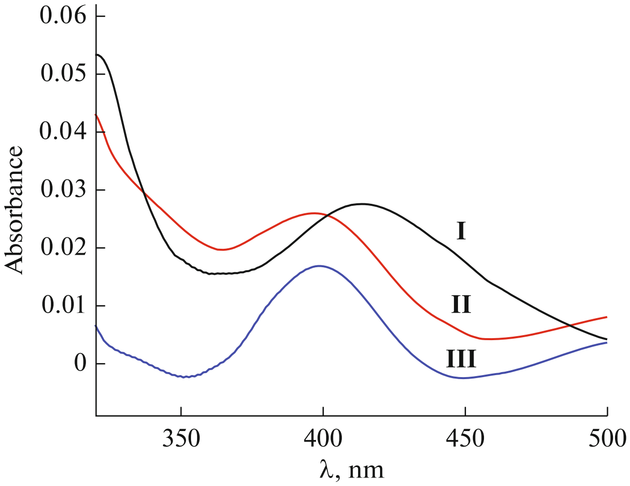


Fig. 2. Ultraviolet spectroscopy of **I**, **II**, and **III**.

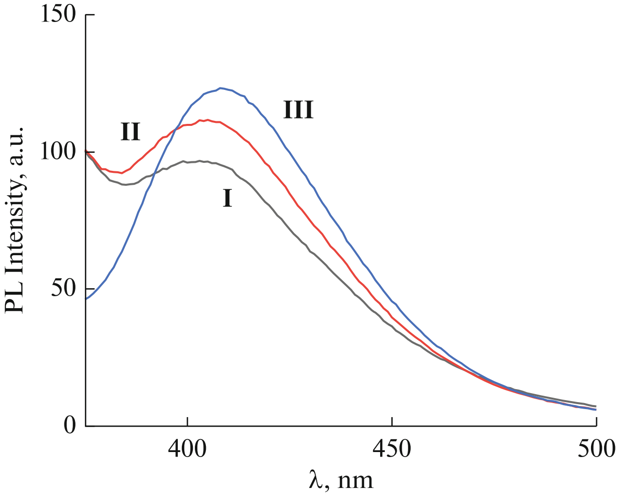


Fig. 3. Fluorescence spectroscopy of **I**, **II**, and **III**.

ysis, mass spectrum. **I** and **III** have also been characterized by single-crystal X-ray diffraction analysis. The UV and fluorescent spectra properties of the compounds **I**, **II** and **III** have been tested.

FUNDING

This work was supported by the Department of Science and Technology Research Projects of Shangrao City (no. SKB2021005), the National Natural Science Foundation of China (no. 62065016), the Natural Science Foundation of Jiangxi Province (no. 20202BABL202023), Innovation Training Program of Shangrao Normal University (no. 202310416002) and the Science and Technology Project of Education Department of Jiangxi Province (no. GJJ190883, GJJ211707).

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

REFERENCES

1. Shi, C., Sun, H.B., Tang, X., et al., *Angew. Chem. Int. Ed.*, 2013, vol. 52, no. 50, p. 13434.
2. Stogniy, M.Y., Bogdanova, E.V., Anufriev, S.A., et al., *Russ. J. Inorg. Chem.*, 2022, vol. 67, no. 10, p. 1537. https://doi.org/10.1134/S0036023622600848
3. Sivaev, I.B., *Russ. J. Inorg. Chem.*, 2021, vol. 66, no. 9, p. 1289. https://doi.org/10.1134/S0036023621090151
4. Matveev, E.Y., Avdeeva, V.V., Zhizhin, K.Y., et al., *Inorganics*, 2022, vol. 10, no. 12, p. 238. https://doi.org/10.3390/inorganics10120238
5. Avdeeva, V.V., Malinina, E.A., and Kuznetsov, N.T., *Coord. Chem. Rev.*, 2022, vol. 469, p. 214636. https://doi.org/10.1016/j.ccr.2022.214636
6. Avdeeva, V.V., Garaev, T.M., Malinina, E.A., et al., *Russ. J. Inorg. Chem.*, 2022, vol. 67, no. 1, p. 28. https://doi.org/10.1134/S0036023622010028
7. Harriman, A., Alamiry, M.A.H., Hagon, J.P., et al., *Angew. Chem. Int. Ed.*, 2013, vol. 52, no. 26, p. 6611.
8. Zhu, L., Lv, W., Liu, S.J., et al., *Chem. Commun.*, 2013, vol. 49, no. 90, p. 10638.
9. Shi, C., Sun, H.B., and Jiang, Q.B., *Chem. Commun.*, 2013, vol. 49, no. 42, p. 4746.
10. Wee, K.R., Han, W.S., Cho, D.W., et al., *Angew. Chem. Int. Ed.*, 2012, vol. 51, no. 11, p. 2677.
11. Kokado, K., Tokoro, Y., and Chujo, Y., *Macromolecules*, 2009, vol. 42, no. 23, p. 9238.
12. Kim, T., Kim, H., Lee, K.M., et al., *Inorg. Chem.*, 2013, vol. 52, no. 1, p. 160.
13. Glukhov, I.V., Antipin, M.Y., and Lyssenko, K.A., *Eur. J. Inorg. Chem.*, 2004, vol. 7, p. 1379.
14. Kokado, K. and Chujo, Y., *Macromolecules*, 2009, vol. 42, no. 5, p. 1418.
15. Wang, R.X., Wang, S.W., and Qi, Y.J., *Chin. J. Inorg. Chem.*, 2012, vol. 28, no. 3, p. 536.
16. Zhang, Q., Han, Y., and Jiao, Y.H., *Chin. J. Inorg. Chem.*, 2016, vol. 32, no. 1, p. 121.
17. Ye, H.D., Zhang, X.Y., Xiao, X., et al., *Chin. J. Inorg. Chem.*, 2021, vol. 37, no. 8, p. 1375.
18. Ye, H.D., Xing, Z.S., Hu, J.R., et al., *Chin. J. Inorg. Chem.*, 2015, vol. 31, no. 8, p. 1534.
19. Sheldrick, G.M., *SHELXS-97, Program for the Solution of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
20. Sheldrick, G.M., *SHELXL-97, Program for the Refinement of Crystal Structures*, Göttingen: Univ. of Göttingen, 1997.
21. Zhang, J.S. and Jin, G.X., *Inorg. Chem. Commun.*, 2008, vol. 11, no. 2, p. 145.
22. Ye, H.D., Zhan, Y.L., Liang, J., et al., *Russ. J. Coord. Chem.*, 2018, vol. 44, no. 7, p. 454.
23. Li, Y., Zou, X.Z., Qiu, W.D., et al., *Chin. J. Inorg. Chem.*, 2019, vol. 35, no. 2, p. 329.