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LETTERS TO THE EDITOR

Reactions of $PtCl_4$ and Na_2PtCl_6 with 18-Crown-6 and Dibenzo-18-crown-6 in Various Solvents

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In this work, we studied the reactions of $PtCl_4$ and Na_2PtCl_6 with 18-crown-6 (L_1) and dibenzo-18-crown-6 (L_2) in acetonitrile, nitromethane, and 1,2-dichloroethane.

Preliminary manipulations and syntheses were carried out using Schlenk technique in dry argon or in a vacuum [1]. Compounds **I**–**IV** were obtained by the reaction of $PtCl_4$ and L_1 in nitromethane and acetonitrile, and compound **V**, by the reaction of $PtCl_4$ and L_2 in nitromethane. The reactions of Na_2PtCl_6 with L_1 and L_2 in acetonitrile yielded complexes **VI** and **VII**.

The formation of the complexes was proved by comparison of the IR spectra of the starting compounds ($PtCl_4$, Na_2PtCl_6, L_1, and L_2) and products **I**–**VII** [2–4]. The cleavage of crown rings in **I** and **III** could be inferred from the absorption bands ν(PtO) ∼448 and 436 cm^{-1}, and also from the absorption band $\nu(CH_2)$, which is shifted upon ring opening to ∼1462 cm^{-1}. In the case of **V**, we found that the $\nu(CH_2)$ absorption bands are split: ∼1452 and ∼1462 cm^{-1} for closed and open methylene chains, respectively, which is caused by the presence of both molecules of the initial crown ether L_2 and its various fragments in the complex. It is also confirmed by the appearance of the absorption band ν(PtO) ∼457 cm^{-1}. Furthermore, the absorption band at ∼620 cm^{-1} corresponding to ν(CCl) was found in **V**. It can be assigned to the chloroethyl substituent at the benzene ring (L_2-CH_2CH_2Cl), also arising from cleavage of the macrocycle. In **VI** and **VII**, ν_s(COC) decreases by 20 and 14 cm^{-1}, respectively, compared to the same vibrations of free L_1 and L_2 [5]. The frequency $\nu(CH_2)$ in **VI** decreases by 40 cm^{-1}, and in **VII** it increases by 35 cm^{-1}. The coordination of the sodium cation by the macrocycle is confirmed by the appearance of the absorption bands ν(NaO) ∼280 and 467 cm^{-1} for **VI** and **VII**, respectively, and also by the shift of the ν_{as}(COC) band by ∼4–8 cm^{-1}.

Depending on a medium used for the reaction, compounds **I**–**VII** incorporate both organic and inorganic cations. In particular, the bands characteristic of $\nu(OH_3^+)$ (∼1664, 1576 and 1700, 1508 cm^{-1}, respectively) are found in the IR spectra of **II** and **IV**, whereas the stretching vibrations of coordinated $(H_2Cl)^+$ (∼2312 cm^{-1}) are observed in the case of **II**. The IR spectrum of compound **I** prepared in nitromethane contains the $\delta(NH_2)$ band at ∼1568 cm^{-1} originating from the reduction of CH_3NO_2 to CH_3NH_2 and its coordination through the nitrogen atom [ν(PtN) ∼424 cm^{-1}]. For **V**, we found the absorption bands $\delta(NH_3^+)$ ∼1560 and 1304 cm^{-1}, and also $\nu(NH_3^+)$ ∼3000 cm^{-1} and one $\delta(CH_2)$ band at ∼1420 cm^{-1}, characteristic of the methylene group connected to the electrophilic nitrogen atom $\equiv N^+–$. This may be due to the fact that the $CH_3NH_3^+$ cation enters the macrocycle cavity. We also found that acetonitrile molecules enter the composition of **III**, **VI**, and **VII**, which is proved by the presence of the absorption bands ν(CN) ∼2150, 2248, and 2264 cm^{-1}, respectively, and $\delta(CH_3–CN)$ ∼382 cm^{-1} in their IR spectra.

The bands ∼339, 304 (in **III** and **IV**), ∼332, 304 (in **I** and **V**), and ∼324 cm^{-1} (in **II**, **VI**, and **VII**) can be assigned to ν(PtCl) stretching vibrations. The bridging Pt–Cl–Pt bonds were found in compounds **I**–**VI** (absorption bands ∼248 and 269 cm^{-1}, respectively). Complexes **I** and **III** also contain molecules of water of crystallization and of coordinated water: δ(HOH) ∼1632 and 1648 cm^{-1}, respectively. Water of crystallization was also found in **V** [δ(HOH) ∼1630 cm^{-1}] in addition to a fragment with a Pt–OH bond, ν ∼476 cm^{-1}. In the range 3500–3200 cm^{-1}, there are sharp and smoothed peaks, which confirms the presence of water molecules and hydroxyl in **V**.

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On the basis of the elemental, X-ray fluorescence, and derivatographic analyses, we can assign the following compositions to **I**–**VII**.

$[2(PtCl_3 \cdot CH_3NH_2 \cdot C_6H_{12}O_4)^+ \cdot (Pt_2Cl_6)^{2-}] \cdot H_2O$ (**I**), mp 134°C. Found, %: C 10.72; H 1.98; Cl 26.98; N 0.89; Pt 37.00. $C_{14}H_{31}Cl_{12}NO_5Pt_3$. Calculated, %: C 10.62; H 1.96; Cl 26.93; N 0.88; Pt 36.97. Total weight loss and solid residue (found, calculated): 37.8, 37.28% and 62.2, 62.72%, respectively.

$[2\{(H_2Cl)^+ \cdot L_1\}^+ \cdot \{Pt_2Cl_{10}\}^{2-}] \cdot 2(OH_3Cl)$ (**II**), mp 128°C. Found, %: C 19.77; H 3.98; Cl 34.11; Pt 26.77. $C_{24}H_{58}Cl_{14}O_8Pt_2$. Calculated, %: C 19.77; H 3.98; Cl 34.11; Pt 26.77. Total weight loss and solid residue (found, calculated): 72.95, 72.87% and 27.05, 29.13%, respectively.

$[(PtCl_2 \cdot CH_3CN \cdot H_2O \cdot C_{10}H_{20}O_6)^{2+} \cdot (Pt_2Cl_{10})]^{2-} \cdot 3(CH_3CN)$ (**III**), mp 132°C. Found, %: C 15.12; H 2.38; Cl 29.81; N 3.92; Pt 40.94. $C_{18}H_{34}Cl_{12}N_4O_7Pt_3$. Calculated, %: C 15.12; H 2.38; Cl 29.81; N 3.92; Pt 40.94. Total weight loss and solid residue (found, calculated): 49.18, 49.1% and 50.82, 50.9%, respectively.

$[3\{(OH_3)^+ \cdot L_1\}^+ \cdot \{Pt_2Cl_{10}\}^{2-} \cdot \{PtCl_5 \cdot CH_3CN\}] \cdot 5(CH_3CN)$ (**IV**), mp 127°C. Found, %: C 26.03; H 4.47; Cl 24.66; N 3.83; Pt 26.44. $C_{48}H_{99}Cl_{15}N_6O_{21}Pt_3$. Calculated, %: C 26.03; H 4.47; Cl 24.56; N 3.80; Pt 26.44. Total weight loss and solid residue (found, calculated): 73.58, 73.50% and 26.42, 26.50%, respectively.

$[4\{(CH_3NH_3)^+ \cdot (L_2–CH_2CH_2Cl)\}]^+ \cdot [\{PtCl_3 \cdot (OH^-)\}^{2-} \cdot (Pt_2Cl_{10})^{2-}] \cdot H_2O$ (**V**), mp 198°C. Found, %: C 38.04; H 4.25; Cl 20.47; N 1.9; Pt 20.18. $C_{92}H_{123}Cl_{17}N_4O_{26}Pt_3$. Calculated, %: C 38.08; H 4.24; Cl 20.81; N 1.93; Pt 20.18. Total weight loss and solid residue (found, calculated): 74.43, 74.89% and 25.57, 25.11%, respectively.

$[2(Na^+) \cdot (L_1) \cdot (CH_3CN) \cdot (H_2O)]^+ \cdot [Pt_2Cl_{10}]^{2-}$ (**VI**), mp 149°C. Found, %: C 15.12; H 2.62; Cl 31.91; N 1.28; Na 4.14; Pt 35.01. $C_{14}H_{29}Cl_{10}NNa_2O_7Pt_2$. Calculated, %: C 15.10; H 2.60; Cl 31.88; N 1.26; Na 4.13; Pt 35.01. Total weight loss and solid residue (found, calculated): 54.8, 54.52% and 45.2, 45.48%, respectively.

$[2(Na^+ \cdot L_2) \cdot 3(CH_3CN) \cdot (H_2O)]^+ \cdot [PtCl_6]^{2-}$ (**VII**), mp 175°C. Found, %: C 41.98; H 4.49; Cl 16.23; N 3.21; Na 3.52; Pt 14.83. $C_{46}H_{59}Cl_6N_3Na_2O_{13}Pt$. Calculated, %: C 41.98; H 4.49; Cl 16.20; N 3.19; Na 3.50; Pt 14.83. Total weight loss and solid residue (found, calculated): 73.6, 73.57% and 26.4, 26.43%, respectively.

The IR spectra of the substances in the range 4000–400 cm^{-1} were taken in Nujol on a Perkin–Elmer IR-16PC-FF spectrophotometer and in the range 500–200 cm^{-1} on a Specord M-80 spectrophotometer. Elemental analysis was carried out on a Carlo Erba analyzer. The metal content was determined by the X-ray fluorescence method on a VRA-20L device. The chlorine content was determined according to [6]. The thermograms of the compounds were recorded on a Paulik–Paulik–Erdey Q-1500D derivatograph (sample weight 50–60 mg, heating rate 10 deg/min).

REFERENCES

1. Bulychev, B.M. and Bel'skii, V.K., *Zh. Neorg. Khim.*, 1995, vol. 40, no. 11, p. 1834.
2. Matsuura, H. and Miyazawa, T., *Bull. Chem. Soc. Jpn.*, 1968, vol. 75, no. 9, p. 865.
3. Nakamoto, K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, New York: Wiley, 1986.
4. Kazitsyna, L.A. and Kupletskaya, N.B., *Primenenie UF-, IK- i YaMR-spektroskopii v organicheskoi khimii* (Applications of UV, IR, and NMR Spectroscopy to Organic Chemistry), Moscow: Vysshaya Shkola, 1971.
5. Tsivadze, A.J., Varnek, A.A., and Khutorskii, V.E., *Koordinatsionnye soedineniya metallov s kraun-ligandami* (Coordination Compounds of Metals with Crown Ligands), Moscow: Nauka, 1991.
6. *Metody kolichestvennogo organicheskogo elementnogo mikroanaliza* (Methods of Quantitative Organic Elemental Microanalysis), Gel'man, A.I., Ed., Moscow: Khimiya, 1987, pp. 230–231.