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Platinum(II) Cationic Complexes with Derivatives of 2-Acyl-1,3-Cyclopentanedions

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Abstract—*cis*-Diammineplatinum(II) complexes containing 2-acyl-1,3-cyclopentadion fragments as a bidentate acido ligand were prepared by the transformation of *cis*-diamminediiodoplatinum(II) to *cis*-diamminesulfatoplatinum(II) under the action of silver sulfate with the subsequent treatment of the resulting complex by barium hydroxide and by the reaction of the synthesized base with a twofold amount of 2-acyl-1,3-cyclopentanedion. The products are the cationic complexes of *cis*-diammineplatinum(II) and contain 2-acyl-1,3-cyclopentanedionate as a bidentate acido ligand, which chelates platinum atom by the carbonyl groups of side acyl chain and one group connected with five-membered cycle, whereas a 2-acyl-1,3-cyclopentadion enolate anion forms counter ion.
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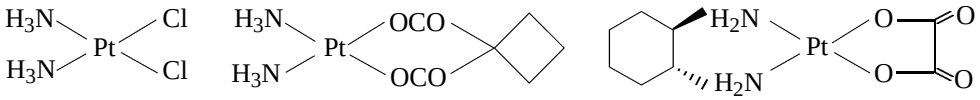
Discovery of strong antineoplastic properties of *cis*-dichlorodiammineplatinum(II) (cislatine), the inorganic compound known even in XIX century, again caused an interest to complexes of metals, in particular of platinum [1]. Intensive search for new antineoplastic substances among the platinum complex compounds begun and the study of the mechanism of their action was launched. At present a number of antineoplastic drugs [*cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II) (carboplatine), (*trans*-L-1,2-diaminocyclohexane)oxalatoplatinum(II) (oxaliplatine), etc.] have been elaborated on the basis of platinum(II) coordination compounds, which are effectively used in treatment of oncology diseases. Among these compounds, cisplatine still belongs to antineoplastic drugs most widely used for antineoplastic chemotherapy of cancer (in particular, for especially heavy metastasis forms) [2–4].



Cisplatine Carboplatine Oxaliplatine

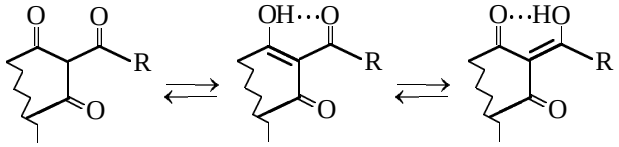
Alongside with effective oncological action, cisplatine is rather toxic, in particular with respect to nephrosis, which is badly transmitted. It is poorly soluble in water and can be administered only intravenously for a long period; for certain tumors development of resistency is observed. It has been found that the high toxicity is caused basically by the formation of toxic oligomers at hydrolysis of *cis*-dichlorodiammineplatinum(II), and the replacement of chlorine atoms by ligands strongly bound to platinum(II) reduces toxicity and increases solubility in water.

Compared to normal cells, tumoral cells are characterized by a higher level of DNA synthesis, whereas DNAs are macromolecules at which the action of some antineoplastic drugs is directed, in particular of alkylating substances. It has been shown that platinum(II) complexes possessing an antineoplastic action are alkylating compounds which selectively suppress the synthesis of DNA, but affect the synthesis of RNA and proteins only slightly. Thus, one of principal causes of the antineoplastic action of platinum complexes is the inhibition of DNA copying [5].

Platinum(II) can also be bound to endocellular thiols, among which there are cytoplasmic non-protein thiol glutathione and the main fraction of cytoplasmic protein thiols, metalthioneines. As a result of this concurrent reaction, inactive particles are formed and resistance to this chemical develops [6].

Thus, the inclusion of platinum(II) compounds preventing deactivations on the reaction with endocellular thiols in complexes and the replacement of chlorine atoms in the inner sphere of *cis*-dichlorodiammineplatinum(II) by acido ligands capable of forming compounds with strong chelated platinum(II) shall result in the reduction of toxicity and also can promote overcoming resistance development.

Last years cyclic β,β'-triketones and their derivatives find significant application in organic synthesis, including the preparation of biologically active materials, that is connected with rich synthetic opportunities of the multifunctional β,β'-tricarbonyl systems in these compounds, which can be considered as rather universal block-synthons in full syntheses of steroids, certain antibiotics, pheromones, prostaglandins, medicines, etc., depending on the structure of a cyclic part of a molecule and a side acyl chain [7–10]. A structural fragment of 2-acyl-1,3-cycloalkanedions (**I**) with a strong intramolecular bond existing as *endo* and/or *exo* keto-enol tautomers enters in one or another form into the composition of many bioactive compounds produced by various plants, microorganisms, insects, and also of synthesized compounds [11]. The presence of an enolized carbonyl group and a conjugated carbonyl group in the β,β'-position causes an opportunity of the participation of tricarbonyl compounds in chelation with transition metals that allows considering them as bidentate acido ligands.

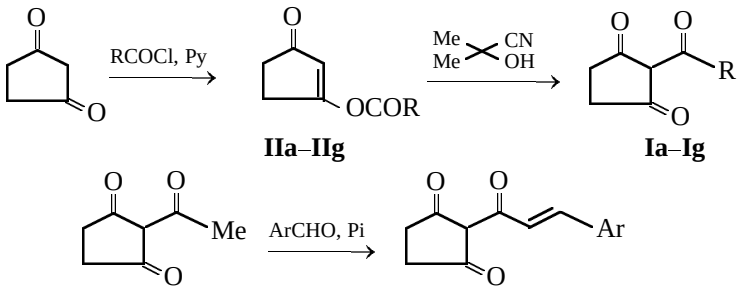


I

It seems promising for the expanding therapeutic action and for increasing the efficiency of platinum(II) coordination compounds to introduce in their composition fragments of β,β'-triketones of natural and allied structure, which in some cases possess antineoplastic properties alongside with antibiotic, hypotensive, and other kinds of useful activity.

In view of the above-stated we have offered the approach [12, 13] to the synthesis of new cationic *cis*-diammineplatinum(II) complexes with the use of derivatives of biologically active 2-acyl-1,3-cyclopentanedions as bidentate acido ligands, which exist in the form of enol tautomers with a strong chelating intramolecular bond and show properties of acid vinilog.

To obtain β,β'-triketones of cyclopentane series **Ia**–**Ig** with the structure allowing these compounds to be included in platinum(II) coordination compounds, we used the method of O–C isomerization of corresponding enolacylates under the action of acetonecyanohydrine in the presence of triethylamine in absolute acetonitrile [8]. Enolacylates **IIa**–**IIg** were synthesized by direct *O*-acylation of cyclopentane-1,3-dion by acid chlorides of carboxylic acids in the presence of pyridine in absolute chloroform [14].



IIa–**IIg** **Ia**–**Ig**

Ia **Ih**–**Ik**, R = CH=CHAr

I, R = Me (**a**), Et (**b**), Oct (**c**), Ph (**d**), C_6H_4OMe-4 (**e**), $C_6H_3(OMe)_2$-3,4 (**f**), C_6H_4Ph-4 (**g**); Ar = Ph (**h**), C_6H_4Me-4 (**i**), C_6H_4OMe-3 (**j**), C_6H_4COOMe-4 (**k**); **II**, R = Me (**a**), Et (**b**), Oct (**c**), Ph (**d**), C_6H_4OMe-4 (**e**), $C_6H_3(OMe)_2$-3,4 (**f**), C_6H_4Ph-4 (**g**).

Reactivity of the methylene group in the side chain of cyclic β,β'-triketones is somewhat reduced because of the participation of the carbonyl group in the chelate formation. However, 2-acetyl-1,3-cycloalkanedions enter to the Claisen-Schmidt condensation with aromatic aldehydes and form β,β'-tricarbonyl com-

pounds with unsaturated side acyl chain showing hypotensive and other kinds of activity [15–17].

Therefore we have carried out the synthesis of 2-(3-aryl-acryloyl)-1,3-cyclopentadions **Ih**–**Ik**, R = CH=CHAr by condensation of 2-acetyl-1,3-cyclopentanedion **Ia** with aromatic aldehydes in the presence of piperidine in absolute benzene at reflux. The yield of the obtained compounds reaches 61–68%.

To determine and prove the structure of synthesized compounds **Ia**–**Ilk** and **IIa**–**IIg**, we used ^{1}H NMR and IR spectroscopy. A strong absorption band in the range 1680–1720 cm^{-1} (absorption of the conjugated carbonyl group) and two rather narrow absorption bands in the region of 1565–1655 cm^{-1} are observed in the IR spectra of all obtained β,β'-triketones **Ia**–**Ik**. The band separation can be caused by the difference in absorption of chelating carbonyl group and the enol double bond, or two bands can correspond to chelating carbonyl groups of various enol–enol tautomers [18]. In the last case the high-frequency band corresponds to the carbonyl group connected to the cyclopenane ring, i.e. it corresponds to the structure of the enol with the enolyzed carbonyl group in the side chain. The low-frequency band is caused by the absorption of a chelating carbonyl group of a side chain. In the ^{1}H NMR spectra along with all necessary resonance signals of protons of methyl and methylene groups (for compounds **Ih**–**Ik** the signals of vinyl protons at δ 7.9–8.0 ppm and aromatic protons at 7.50–8.10 ppm), in the low-field region (~14–16 ppm) a signal of the enol proton was found that points to the presence of a strong intramolecular hydrogen bond.

Several procedures for the synthesis of platinum(II) carboxylate complexes have been described in the literature [19–21]. Two main procedures are given by Eqs. (1), (2) and (3), (4), respectively.

$$cis\text{-}PtA_2I_2 + 2AgNO_3 \longrightarrow cis\text{-}[PtA_2(H_2O)_2](NO_3)_2 + 2AgI, \quad (1)$$

$$cis\text{-}[PtA_2(H_2O)_2](NO_3)_2 + 2NaX \longrightarrow cis\text{-}PtA2X2 + 2NaNO_3, \quad (2)$$

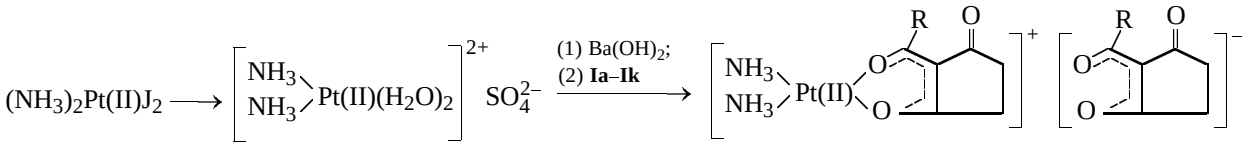
$$cis\text{-}PtA_2I_2 + Ag_2SO_4 \longrightarrow cis\text{-}[PtA_2(H_2O)_2](SO_4) + 2AgI, \quad (3)$$

$$cis\text{-}[PtA_2(H_2O)_2](SO_4) + BaX_2 \longrightarrow cis\text{-}PtA_2X_2 + 2BaSO_4. \quad (4)$$

Here A_2 is a bidentate amine or two monodentate amines, X is a bidentate ligand or two monodentate carboxylaled ligands, and *cis*-PtA_2I_2 is obtained by Dhara's method [22].

The drawbacks of the first method are a low yield, a significant duration of the reaction, and a difficulty to remove the water-soluble sodium nitrate. The application of the second method for our purposes was limited by a low solubility of barium salts of 2-acyl-1,3-cyclopentanedions in water and organic solvents.

We synthesized the *cis*-diammineplatinum(II) complexes **IIIa**–**IIIk** containing fragments of 2-acyl-1,3-cyclopentadions as acido ligands by the transformation of *cis*-diiodododiammineplatinum(II) to *cis*-sulfatodiammineplatinum(II) under the action of silver sulfate with the subsequent treatment of this latter by barium hydroxide and the treatment of the resulting base with a twofold excess of 2-acyl-1,3-cyclopentadion **Ia**–**Ik**, yield was 65–85%.



IIIa–**IIIk**

III, R = Me (**a**), Et (**b**), Oct (**c**), Ph (**d**), C_6H_4OMe-4 (**e**), $C_6H_3(OMe)_2$-3,4 (**f**), C_6H_4Ph-4 (**g**), CH=CHPh (**h**), CH=CH·C_6H_4Me-4 (**i**), CH=CHC_6H_4OMe-3 (**j**), CH=CHC_6H_4COOMe-4 (**k**).

In view of the data recently published for the new cationic platinum(II) complexes [23, 24], and also on the basis of the data of elemental analysis, and ^{1}H NMR and IR spectroscopy for the obtained compounds we propose the structure of *cis*-diammineplatinum(II) cationic complexes **IIIa**–**IIIk**. The ^{1}H NMR spectra show that fragments of two molecules of the starting triketone enter into composition of the synthesized platinum(II) complexes. The complexes contain 2-acyl-1,3-cyclopentanedionate chelated with a platinum(II) atom by means of a carbonyl group in a side acetyl chain and a carbonyl group connected to a five-membered cycle, whereas enolate anion of 2-acyl-1,3-cyclopentadion is a counter ion. In the ^{1}H

NMR spectra there are resonance signals of all protons of two above-mentioned fragments. Because of significant descreening effect the signals of the side chain protons and the methylene groups of the five-membered ring of the chelating 2-acyl-1,3-cyclopentadionate are observed downfield to the signals of protons of similar groups of the 2-acyl-1,3-cyclopentadion enolate anion. No signals of hydroxyl protons of starting β,β'-triketones are present in the spectra either. In the region of δ 6.52–6.70 (Py-d_5), δ 4.64–4.68 (CD_3OD), and δ 4.82–5.00 ppm (Me_2SO-d_6) in the ^1H NMR spectra of complexes **IIIa**–**IIIk** recorded in various solvents there are the signals of six protons of the two ammonia molecules connected with the platinum atom in the *cis*-position. The IR spectra of the synthesized platinum(II) complexes are characterized by the presence of absorption bands of carbonyl groups of an acido ligand and a counter ion in the field of 1560–1710 cm^{-1}, and also absorption bands of the ammine ligand in the region of 2900–3230 cm^{-1}. The absorption band characteristic of the cyclopentane β,β'-triketones corresponding to the conjugated carbonyl not included to the chelated system do not occur in the region of 1720 cm^{-1} of the IR spectra. The analytical data for the prepared platinum(II) complexes **IIIa**–**IIIk** agree with the proposed general structure.

EXPERIMENTAL

The IR spectra were obtained on a UR-20 spectrometer in KBr for crystalline substances or films for oily substances. The ^1H NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$, Me_2SO-d_6, CD_3OD, and Py-d_5 with TMS as an internal reference and in D_2O with 2,2-dimethyl-2-silapentane-5-sulfoacid as an the internal reference.

The melting and decomposition points were measured on a Boetius heating table.

The reaction courses and the purity of the synthesized products were monitored by ™LC on Silufol UV-254 plates.

2-Acyl-1,3-cyclopentanedions Ia–**Ig** were obtained by the technique [8]. Recrystallization from an ether–hexane mixture, 3:1, colorless crystalline substances.

2-Acyl-1,3-cyclopentanedion (Ia). Yield 72%, mp 72–75°C. IR spectrum, ν, cm^{-1}: 1595, 1655, 1715. ^1H NMR spectrum (CD_3OD), δ, ppm: 2.44 s [3H, $C(O)CH_3$], 2.64 s (4H, $2CH_2$ cycl.). ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.40 s [3H, $C(O)CH_3$], 2.56 s (4H, $2CH_2$ of cycle).

2-Propinyl-1,3-cyclopentanedion (Ib). Yield 62%, mp 75–77°C. IR spectrum, ν, cm^{-1}: 1605, 1645, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 t [3H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 2.54 m (2H, CH_2 cycl.), 2.78 m (2H, CH_2 cycl., 2.98 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 14.08 br.s (1H, OH enol.).

2-Octanoyl-1,3-cyclopentanedion (Ic). Yield 67%, mp 23–24°C. IR spectrum, ν, cm^{-1}: 1605,1645, 1720. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 m (3H, CH_2CH_3), 1.30 m (8H, $4CH_2$), 1.62 quintet [2H, $C(O)CH_2CH_2CH_2$, ^3J 7.0 Hz], 2.50 m (2H, CH_2 cycl.), 2.74 m (2H, CH_2 cycl.), 2.92 t [2H, $C(O)CH_2CH_2$, ^3J 7.0 Hz], 14.88 br.s (1H, OH enol.). ^1H NMR spectrum (CD_3OD), δ, ppm: 0.90 m (3H, CH_2CH_3), 1.30 m (8H, $4CH_2$), 1.62 quintet [2H, $C(O)CH_2CH_2 \cdot CH_2$, ^3J 7.0 Hz], 2.63 s (4H, $2CH_2$ cycl.), 2.88 t [2H, $C(O)CH_2CH_2$, ^3J 7.0 Hz], 15.35 w. s (1H, OH enol.).

2-Benzoyl-1,3-cyclopentanedion (Id). Yield 65%, mp 45–47°C. IR spectrum, ν, cm^{-1}: 1580, 1635, 1680. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.60 s (2H, CH_2 cycl.), 2.84 s (2H, CH_2 cycl.), 7.50 m (2H, H arom.), 7.62 m (1H, H arom.), 8.08 m (2H, H arom.), 15.40 br.s (1H, OH enol.).

2-(3-Methoxybenzoyl)-1,3-cyclopentanedion (Ie). Yield 60%, mp 78–80°C. IR spectrum, ν, cm^{-1}: 1580, 1635, 1680. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.62 m (2H, CH_2 cycl.), 2.87 m (2H, CH_2 cycl.), 3.88 s (3H, OCH_3), 7.18 m (1H, H arom.), 7.40 m (1H, H arom.), 7.70 m (2H, H arom.), 15.80 br.s (1H, OH enol.).

2-(3,4-Dimethoxyphenylacetyl)-1,3-cyclopentanedion (If). Yield 87%, oily substance. IR spectrum, ν, cm^{-1}: 1545, 1610, 1710. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.56 m (2H, CH_2 cycl.), 2.76 m (2H, CH_2 cycl.), 3.89 s (6H, $2OCH_3$), 4.18 s [2H, $C(O)CH_2Ar$], 6.86 m (3H, H arom.), 15.80 br.s (1H, OH enol.).

2-(4-Phenylbenzoyl)-1,3-cyclopentanedion (Ig). Yield 86%, mp 154–156°C. IR spectrum, ν, cm^{-1}: 1580, 1610, 1700. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.62 m (2H, CH_2 cycl.), 2.87 m (2H, CH_2 cycl.), 7.45 m (3H, H arom.), 7.68 m (4H, H arom.), 8.20 m (2H, H arom.), 15.24 br.s (1H, OH enol.).

Condensation of 2-acetyl-1,3-cyclopentanedion with aromatic aldehydes. To a solution 0.01 mol of 2-acetyl-1,3-cyclopentanedion **Ia** in 40 ml of absolute benzene 0.15 mol of piperidine and 0.09 mol of a corresponding aromatic aldehyde were added. The reaction mixture was boiled with a Dyne-Stark trap for 5 h and kept at room temperature. Benzene was removed on a rotary evaporator, a remainder was acidified with hydrochloric acid up to pH 2. The resulting crystalline

condensation product was filtered off, washed with 1 N hydrochloric acid (25 ml), then with water (3× 25 ml), dried in air, and recrystallized from acetone as a yellow crystalline substance. Yield 61–68%.

2-(3-Phenylacriloyl)phenylacriloyl)-1,3-cyclopentanedion (Ih). Yield 67%, mp 108–109°C. IR spectrum, ν, cm^{-1}: 1590, 1635, 1705. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.62 s (4H, $2CH_2$ cycl.), 7.50 m (3H, H arom.), 7.74 m (2H, H arom.), 7.9 q (2H, H vinyl).

2-[3-(4-Methylphenyl)acriloyl]-1,3-cyclopentanedion (Ii). Yield 61%, mp 86–91°C. IR spectrum, ν, cm^{-1}: 1590, 1640, 1700. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.14 s (3H, C_6H_4Me), 2.62 s (4H, $2CH_2$ cycl.), 7.58 d (2H, H arom., ^3J 8.5 Hz), 7.72 d (2H, H arom., ^3J 8.5 Hz), 7.94 m (2H, H vinyl). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.41 s (3H, C_6H_4Me), 2.60 m (2H, CH_2 cycl.), 2.75 m (2H, CH_2 cycl.), 7.25 d (2H, H arom., ^3J 8.5 Hz), 7.60 d (2H, H arom., ^3J 8.5 Hz), 7.94 m (2H, H vinyl).

2-[3-(3-Methoxyphenyl)acriloyl]-1,3-cyclopentanedion (Ij). Yield 68%, mp 112–114°C. IR spectrum, ν, cm^{-1}: 1585, 1640, 1710. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.62 m (2H, CH_2 cycl.), 2.76 m (2H, CH_2 cycl.), 3.86 s (3H, OCH_3), 7.01 m (1H, H arom.), 7.19 m (1H, H arom.), 7.35 m (2H, H arom.), 7.94 m (2H, H vinyl).

2-[3-(4-Methoxycarbonylphenyl)acriloyl]-1,3-cyclopentanedion (Il). Yield 65%, mp 186–188°C. IR spectrum, ν, cm^{-1}: 1575, 1640, 1725. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.65 s (4H, $2CH_2$ cycl.), 3.90 s (3H, $C_6H_4CO_2Me$), 7.85 d (2H, H arom., ^3J 8 Hz), 7.90 d (2H, H arom., ^3J 8 Hz), 8.05 m (2H, H vinyl). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.64 m (2H, CH_2 cycl.), 2.78 m (2H, CH_2 cycl.), 3.96 s (3H, $PhCO_2CH_3$), 7.75 d (2H, H arom., ^3J 8 Hz), 7.99 s (2H, H vinyl), 8.10 d (2H, H arom., ^3J 8 Hz).

3-Acyloxy-2-cyclopentene-1-ons (IIa–IIg) prepared by the procedure [14]. Recrystallization from a diethyl ether-hexane mixture, 2:1, colorless crystalline substances.

3-Acetoxy-2-cyclopentene-1-on (IIa). Yield 75%, oily substance. Identical to an independently synthesized sample [14].

3-Propionyloxy-2-cyclopentene-1-on (IIb). Yield 69%, oily substance. IR spectrum, ν, cm^{-1}: 1165, 1605, 1690, 1720, 1795. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.11 t (3H, $CO_2CH_2CH_3$, ^3J 7.5 Hz), 2.38 m (2H, CH_2 cycl.), 2.64 q (2H, $CO_2CH_2CH_3$, ^3J 7.5 Hz), 2.74 m (2H, CH_2 cycl.), 6.05 m (1H, H vinyl)

3-Octanoyloxy-2-cyclopentene-1-on (IIc). Yield 70%, mp 28–29°C. IR spectrum, ν, cm^{-1}: 1165, 1615, 1690, 1725, 1800. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 0.9 m (3H, CH_2CH_3), 1.34 m (8H, $4CH_2$), 1.71 quintet (2H, $CO_2CH_2CH_2CH_2$, ^3J 7.0 Hz), 2.46 t (2H, $CO_2CH_2CH_2$, ^3J 7.0 Hz), 2.56 m (2H, CH_2 cycl.), 2.76 m (2H, CH_2 cycl.), 6.24 m (1H, H vinyl).

3-Benzoyloxy-2-cyclopentene-1-on (IId). Yield 67%, mp 102–104°C. IR spectrum, ν, cm^{-1}: 1170, 1605, 1690, 1720, 1760. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.52 m (2H, CH_2 cycl.), 2.92 m (2H, CH_2 cycl.), 6.39 m (1H, H vinyl), 7.52 m (2H, H arom.), 7.68 m (1H, H arom.), 8.12 m (2H, H arom.).

3-(3-Methoxybenzoyloxy)-2-cyclopentene-1-on (IIe). Yield 59%, mp 86–89°C. IR spectrum, ν, cm^{-1}: 1170, 1605, 1690, 1720, 1775. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 m (2H, CH_2 cycl.), 2.92 m (2H, CH_2 cycl.), 3.88 s (3H, OCH_3), 6.40 m (1H, H vinyl), 7.20 m (1H, H arom.), 7.43 m (1H, H arom.), 7.62 m (1H, H arom.), 7.74 m (1H, H arom.).

3-(3,4-Dimethoxyphenylacetyloxy)-2-cyclopentene-1-on (IIf). Yield 82%, oily substance. IR spectrum, ν, cm^{-1}: 1170, 1610, 1690, 1720, 1790. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 m (2H, CH_2 cycl.), 2.76 m (2H, CH_2 cycl.), 3.78 s (2H, $CO_2 \cdot CH_2Ar$), 3.88 s (6H, $2OCH_3$), 6.24 m (1H, H vinyl), 6.82 s (1H, H arom.), 6.85 m (2H, H arom.).

3-(4-phenylbenzoyloxy)-2-cyclopentene-1-on (IIg). Yield 71%, mp 184–186°C. IR spectrum, ν, cm^{-1}: 1165, 1665, 1695, 1710, 1750. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.54 m (2H, CH_2 cycl.), 2.94 m (2H, CH_2 cycl.), 6.42 m (1H, H vinyl), 7.36–7.58 m (3H, H arom.), 7.62–7.80 m (4H, H arom.), 8.15–8.26 m (2H, H arom.).

Synthesis of platinum(II) coordination compounds IIIa–IIIk. In a solution of 0.0125 mol with a 3% deficit of silver sulfate in 100 ml of distilled water 0.0125 mol of *cis*-diodidodiammineplatinum(II) was added with stirring. The reaction mixture was stirred for 24 h at room temperature in the dark. A precipitate was filtered off and a suspension of 0.0125 mol of barium hydroxide octahydrate in 60 ml of distilled water was added to a filtrate and stirred for 12 h. The precipitate was filtered off, and the aqueous solution was evaporated by 2/3 of volume on a rotary evaporator [50°C (15 mm Hg)]. To a transparent filtrate a solution 0.025 mol of 2-acyl-1,3-cyclo-pentanedion **Ia–Ik** in 40 ml of EtOH was added dropwise and the mixture was stirred for 24 h in the dark. The solvent was removed on a rotary evaporator [45°C (15 mm Hg)]. The resulting precipitate was washed out with acetone (2×30 ml), diethyl ether (2×30 ml), and

dried in vacuum (≤50oC). Synthesized complexes **IIIa**–**IIIk** represent crystal substances of light yellow color.

***cis*-Diammine-(2-acetyl-1,3-cyclopentadionato)-platinum(II) 2-acetyl-1,3-cyclopentadionate (IIIa).** Yield 65%, decomp. point 240°C (from an ethanol–diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1365, 1435, 1480, 1560, 1590, 1620, 1695, 2830, 2930, 3120. ^1H NMR spectrum (D_2O), δ, ppm: 2.20 s (3H, CH_3CO), 2.22 s (3H, CH_3CO), 2.32 s (4H, $2CH_2$ cycl.), 2.38 m (2H, CH_2 cycl.), 2.52 m (2H, CH_2 cycl.). ^1H NMR spectrum (CD_3OD), δ, ppm: 2.30 m (10H, $2CH_2$ + $2CH_3CO$), 2.44 m (2H, CH_2 cycl.), 2.55 (2H, CH_2 cycl.), 4.68 br.s (6H, 2NH3). ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.00 s (5H, CH_2 cycl. + CH_3CO), 2.12 s (3H, CH_3CO), 2.28 s (2H, CH_2 cycl.), 2.40 m (2H, CH_2 cycl.), 4.90 br.s (6H, $2NH_3$). ^1H NMR spectrum (Py-d_5), δ, ppm: 2.44 s (8H, $4CH_2$ cycl.), 2.84 s (6H, $2CH_3CO$), 6.62 br.s (6H, $2NH_3$). Found, %: C 33.89; H 3.91; N 5.62 Pt 38.30. $C_{14}H_{20}N_2O_6Pt$. Calculated, %: C 33.14; H 3.95; N 5.52; Pt 38.46.

***cis*-Diammine(2-propanoyl-1,3-cyclopentanedionato)platinum(II) 2-propanoyl-1,3-cyclopentanedionate (IIIb).** Yield 73%, decomp. point 205°C (from an ethanol–diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1430, 1480, 1560, 1600, 1680, 1705, 2840, 2945, 2930, 2985, 3150. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 0.92 t [3H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 1.08 t [3H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 2.08 s (4H, $2CH_2$ cycl.), 2.42 m (2H, CH_2 cycl.), 2.52 m (2H, CH_2 cycl.), 2.64 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 2.77 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 4.96 br.s (6H, $2NH_3$). ^1H NMR spectrum (CD_3OD), δ, ppm: 1.02 t [3H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 1.10 t [3H, $C(O)CH_2 \cdot CH_3$, ^3J 7.5 Hz], 2.31 s (4H, $2CH_2$ cycl.), 2.43 m (2H, CH_2 cycl.), 2.54 m (2H, CH_2 cycl.), 2.76 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 2.82 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 4.64 br.s (6H, $2NH_3$). ^1H NMR spectrum (D_2O), δ, ppm: 1.03 t [3H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 1.06 t [3H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 2.41 s (4H, $2CH_2$ cycl.), 2.48 m (2H, CH_2 cycl.), 2.62 m (2H, CH_2 cycl.), 2.73 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz], 2.75 q [2H, $C(O)CH_2CH_3$, ^3J 7.5 Hz]. Found, %: C 35.45; H 4.24; N 5.82 Pt 36.30. $C_{16}H_{24}N_2O_6Pt$. Calculated, %: C 35.88; H 4.48; N 5.23; Pt 36.45.

***cis*-Diammine(2-octanoyl-1,3-cyclopentanedionato)platinum(II) 2-octanoyl-1,3-cyclopentanedionate (IIIc).** Yield 70%, decomp. point 180°C (from an ethanol–diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1430, 1470, 1585, 1605, 1680, 1710, 2860, 2930, 3065. ^1H NMR spectrum (Py-d_5), δ, ppm: 0.80 m (6H, $2CH_2CH_3$), 1.16 m (16H, $8CH_2$), 1.86 quintet [4H, $2C(O)CH_2CH_2CH_2$, ^3J 7.0 Hz], 2.42 s (8H, $4CH_2$ cycl.), 3.38 t [4H, $2C(O)CH_2CH_2$, ^3J 7.0 Hz], 6.70 br.s (6H, $2NH_3$). ^1H NMR spectrum (CD_3OD), δ, ppm: 0.90 m (6H, $2CH_2CH_3$), 1.30 m (16H, $8CH_2$), 1.57 m [4H, $2C(O)CH_2CH_2CH_2$], 2.26–2.50 m (6H, $3CH_2$ cycl.), 2.57 m (2H, CH_2 cycl.), 2.83 t [4H, $2C(O)CH_2CH_2$, ^3J 7.0 Hz], 4.65 br.s (6H, $2NH_3$). ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 0.96 m (6H, $2CH_2CH_3$), 1.23 m (16H, $8CH_2$), 1.53 m [4H, $2C(O)CH_2CH_2CH_2$], 2.42-2.67 m (8H, $4CH_2$ cycl.), 2.74 t [4H, $2C(O)CH_2CH_2$, ^3J 7.0 Hz], 4.82 br.s (3H, NH_3), 4.92 br.s (3H, NH_3). Found, %: C 44.54; H 6.20; N 4.20; Pt 28.97. $C_{26}H_{44}N_2O_6Pt$. Calculated, %: C 46.22; H 6.51; N 4.14; Pt 28.89.

***cis*-diammine(2-benzoyl-1,3-cyclopentanedionato)platinum(II) 2-benzoyl-1,3-cyclopentanedionate (IIId).** Yield 85%, decomp. point 176°C (from an ethanol–diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1430, 1460, 1525, 1560, 1590, 1605, 1665, 1710, 2830, 2930, 3065, 3230. ^1H NMR spectrum (D_2O), δ, ppm: 2.46 s (4H, $2CH_2$ cycl.), 2.49 m (2H, CH_2 cycl.), 2.62 m (2H, CH_2 cycl.), 7.37–7.74 m (10H, H arom.). ^1H NMR spectrum (CD_3OD), δ, ppm: 2.46 s (4H, $2CH_2$ cycl.), 2.54 m (4H, $2CH_2$ cycl.), 4.64 br.s (6H, $2NH_3$), 7.28-7.50 m (5H, H arom.), 7.52–7.70 m (5H, H arom.). ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.11 s (4H, $2CH_2$ cycl.), 2.48 s (4H, $2CH_2$ cycl.), 4.90 br.s (3H, NH_3), 5.00 br.s (3H, NH_3), 7.23–7.62 m (10H, H arom.). ^1H NMR spectrum (Py-d_5), δ, ppm: 2.54 s (8H, $4CH_2$ cycl.), 6.52 br.s (6H, $2NH_3$), 7.40 m (6H, H arom.), 8.14 m (6H, H arom.). Found, %: C 46.01; H 4.18; N 3.9; Pt 30.88. $C_{24}H_{24}N_2O_6Pt$. Calculated, %: C 45.64; H 3.80; N 4.44; Pt 30.90.

***cis*-Diammine[2-(3-methoxybenzoyl)-1,3-cyclopentanedionato]platinum(II) 2-(3-methoxybenzoyl)-1,3-cyclopentanedionate (IIIe).** Yield 66%, decomp. point 165°C (from an ethanol-diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1445, 1525, 1565, 1665, 1710, 2840, 3080. ^1H NMR spectrum (D_2O), δ, ppm: 2.48 s (4H, $2CH_2$ cycl.), 2.52 m (2H, CH_2 cycl.), 2.64 m (2H, CH_2 cycl.), 3.85 s (6H, $2OCH_3$), 7.08–7.30 m (6H, H arom.), 7.41 m (2H, H arom.). ^1H NMR spectrum (CD_3OD), δ, ppm: 2.41 s (4H, $2CH_2$ cycl.), 2.54 m (4H, $2CH_2$ cycl.), 3.79 s (3H, OCH_3), 3.82 s (3H, OCH_3), 4.67 br.s (6H, $2NH_3$), 7.00 m (1H, H arom.), 7.14 m (3H, H arom.), 7.27 m (4H, H arom.). ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.12 s (4H, $2CH_2$ cycl.), 2.16 s (4H, $2CH_2$ cycl.), 3.76 s (3H, OCH_3), 3.80 s (3H, OCH_3), 4.91 br.s (3H, NH_3), 5.02 br.s (3H, NH_3), 6.92–7.40 m (8H, H arom.). ^1H NMR spectrum (Py-d_5), δ, ppm: 2.52 s (8H, $4CH_2$ cycl.), 3.64 s (6H, $2OCH_3$), 6.64 br.s (6H, $2NH_3$), 7.00–7.40 m (5H, H arom.), 7.76 m (3H, H

arom.). Found, %: C 44.71; H 3.89; N 4.16; Pt 29.50. $C_{26}H_{28}N_2O_8Pt$. Calculated, %: C 45.15; H 4.05; N 4.05; Pt 28.22.

***cis*-Diammine[2-(3,4-dimethoxyphenylacetyl)-1,3-cyclopentanedionato]platinum(II) 2-(3,4-dimethoxyphenylacetyl)-1,3-cyclopentanedionate (IIIf).** Yield 70%, decomp. point 250°C (from an acetone–diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1455, 1525, 1615, 1685, 2845, 2935. ^1H NMR spectrum (D_2O), δ, ppm: 2.40 s (8H, $4CH_2$ cycl.), 3.82 s (12H, $4OCH_3$), 3.84 s [2H, $C(O)CH_2Ar$], 3.87 s [2H, $C(O)CH_2Ar$], 6.86–7.08 m (6H, H arom.). ^1H NMR spectrum (Me_2SOd_6), δ, ppm: 2.40 br.s (8H, $4CH_2$ cycl.), 3.78 s (12H, $4OCH_3$), 3.82 s [4H, $2C(O)\cdot CH_2Ar$], 5.00 br.s (6H, $2NH_3$), 6.74–7.10 m (6H, H arom.). Found, %: C 45.91; H 4.53; N 3.55; Pt 24.86. $C_{30}H_{36}N_2O_{10}Pt$. Calculated, %: C 46.21; H 4.62; N 3.59; Pt 25.03.

***cis*-Diammine[2-(4-phenylbenzoyl)-1,3-cyclopentanedionato]platinum(II) 2-(4-phenylbenzoyl)-1,3-cyclopentanedionate (IIIg).** Yield 84%, decomp. point 192°C (from an ethanol-diethyl ether mixture). IR spectrum, ν, cm^{-1}: 1430, 1560, 1580, 1605, 1670, 1715, 2840, 2925, 3070. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.34 br.s (8H, $4CH_2$ cycl.), 4.23 br.s (6H, $2NH_3$), 7.43 m (18H, H arom.). ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.16 s (8H, $4CH_2$ cycl.), 4.94 br.s (3H, NH_3), 5.02 br.s (3H, NH_3), 7.34–7.54 m (8H, H arom.), 7.60 s (4H, H arom.), 7.64–7.81 m (6H, H arom.). ^1H NMR spectrum (Py-d_5), δ, ppm: 2.78 s (8H, $4CH_2$ cycl.), 6.62 br.s (6H, $2NH_3$), 7.39 m (6H, H arom.), 7.69 m (8H, H arom.), 8.26 m (6H, H arom.). ^1H NMR spectrum (CD_3OD), δ, ppm: 2.44 s (4H, $2CH_2$ cycl.), 2.57 m (4H, $2CH_2$ cycl.), 4.66 br.s (6H, NH_3), 7.32–7.52 m (6H, H arom.), 7.58–7.78 m (6H, H arom.). Found, %: C 55.00; H 3.99; N 3.70; Pt 25.08. $C_{36}H_{32}N_2O_6Pt$. Calculated, %: C 55.17; H 4.09; N 3.58; Pt 24.90.

***cis*-diammine[2-(3-phenylacriloyl)-1,3-cyclopentanedionato]platinum(II) 2-(3-phenylacriloyl)-1,3-cyclopentanedionate (IIIh).** Yield 78%, decomp. point 215°C (from THF). IR spectrum, ν, cm^{-1}: 1440, 1570, 1595, 1650, 1685, 1705, 2840, 2930, 3075. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.16 s (8H, $4CH_2$ cycl.), 5.02 br.s (6H, $2NH_3$), 7.38 m (4H arom.), 7.52 m (4H, H arom.), 7.68 m (2H, H arom.), 8.16–8.34 m (4H, H vinyl). ^1H NMR spectrum (Py-d_5), δ, ppm: 2.44 s (8H, $4CH_2$ cycl.), 6.64 br.s (6H, $2NH_3$), 7.22 m (6H, H arom.), 7.68 m (4H, H arom.), 8.06 d (2H, H vinyl, ^3J 16 Hz), 9.18 d (2H, H vinyl, ^3J 16 Hz). Found, %: C 49.04; H 4.00; N 4.25; Pt 28.71. $C_{28}H_{28}N_2O_6Pt$. Calculated, %: C 49.19; H 4.10; N 4.10; Pt 28.55.

***cis*-diammine-{2-(3-(4-methylphenyl)acriloyl)-1,3-cyclopentanedionato]}platinum(II) 2-[3-(4-methylphenyl)acriloyl]-1,3-cyclopentanedionate (IIIi).** Yield 74%, decomp. point 195°C (from THF). IR spectrum, ν, cm^{-1}: 1290, 1465, 1560, 1590, 1635, 1670, 1700, 2845, 2930, 3090. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.10 s (3H, C_6H_4Me), 2.13 s (3H, C_6H_4Me), 2.32 m (8H, $4CH_2$ cycl.), 4.95 br.s (6H, $2NH_3$), 7.22 d (2H, H arom., ^3J 8 Hz), 7.34 d (2H, H arom., ^3J 8 Hz), 7.46 d (2H, H arom., ^3J 8 Hz), 7.60 d (2H, H arom., ^3J 8 Hz), 8.14 m (4H, H vinyl). ^1H NMR spectrum (CD_3OD), δ, ppm: 2.36 s (12H, $3CH_2$ cycl. + $2C_6H_4Me$), 2.57 m (2H, CH_2 cycl.), 4.66 br.s (6H, $2NH_3$), 7.20 m (4H, H arom.), 7.54 m (4H, H arom.), 8.10 d (2H, H vinyl, ^3J 16 Hz), 8.23 d (2H, H vinyl, ^3J 16 Hz). Found, %: C 50.45; H 4.40; N 4.13; Pt 27.62. $C_{30}H_{32}N_2O_6Pt$. Calculated, %: C 50.63; H 4.50; N 3.94; Pt 27.43.

***cis*-Diammine{2-[(3-(3-methoxyphenyl)acriloyl)-1,3-cyclopentanedionato]}platinum(II) 2-[3-(3-methoxyphenyl)acriloyl]-1,3-cyclo-pentanedionate (IIIj).** Yield 68%, decomp. point 215°C (from THF). IR spectrum, ν, cm^{-1}: 1290, 1445, 1560, 1590, 1635, 1670, 1715, 2840, 2950, 3090. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.12 s (4H, $2CH_2$ cycl.), 2.42 m (2H, CH_2 cycl.), 2.54 m (2H, CH_2 cycl.), 3.74 s (3H, OCH_3), 3.78 s (3H, OCH_3), 4.95 br.s (6H, $2NH_3$), 7.16 m (2H, H arom.), 7.34–7.62 m (6H, H arom.), 8.26 m (4H, H vinyl). Found, %: C 48.30; H 4.20; N 3.90; Pt 26.40. $C_{30}H_{32}N_2O_8Pt$. Calculated, %: C 48.45; H 4.31; N 3.77; Pt 26.24.

***cis*-Diammine{2-[(3-(4-methoxyphenyl)acriloyl)-1,3-cyclopentanedionato]}platinum(II) 2-[3-(4-methoxycarbonylphenyl)acriloyl]-1,3-cyclopentanedionate (IIIl).** Yield 67%, decomp. point 205°C (from THF). IR spectrum, ν, cm^{-1}: 1290, 1435, 1555, 1590, 1635, 1680, 1720, 2830, 2960. ^1H NMR spectrum (Me_2SO-d_6), δ, ppm: 2.14 s (4H, $2CH_2$ cycl.), 2.40 m (2H, CH_2 cycl.), 2.58 m (2H, CH_2 cycl.), 3.88 s (3H, $C_6H_4CO_2Me$), 3.90 s (3H, $C_6H_4CO_2Me$), 5.00 br.s (6H, $2NH_3$), 7.69 d (2H arom., ^3J 8.5 Hz), 7.80 d (2H arom., ^3J 8.5 Hz), 7.98 d (2H arom., ^3J 8.5 Hz), 8.08 d (2H arom., ^3J 8.5 Hz), 8.20 d (2H vinyl, ^3J 16 Hz), 8.30 d (2H, H vinyl, ^3J 16 Hz). Found, %: C 47.92; H 3.90; N 3.67; Pt 24.57. $C_{32}\cdot H_{32}N_2O_{10}Pt$. Calculated, %: C 48.06; H 4.01; N 3.50; Pt 24.21.

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