Table 1. Indexing was performed by the method of Hess and Lipson [2] from all the reflections in the orthorhombic system with the lattice parameters a = 7.86, b = 7.63, c = 10.79 Å.

DISCUSSION OF RESULTS

By indexing powder photographs in the orthorhombic system we found that the substance is an individual compound. This is the first preparation of a complex compound containing platinum and technetium. As this preparation is easily soluble in hot water, it can be used to prepare bimetallic coating catalysts.

CONCLUSIONS

1. Tetrammonium platinum pertechnetate has been synthesized.

2. Its powder pattern has been indexed in the orthorhombic system and the lattice parameters have been measured.

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3-AMINOCOUMARIN: A NEW LIGAND FOR SYNTHESIS OF POTENTIALLY BIOLOGICALLY ACTIVE COMPLEXES OF THE PLATINUM METALS

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UDC 547.587.51:542.91:541.69:541.49:546.92

In view of the antitumor activity of coordination compounds of the platinum metals [1], the known biological action of coumarin and its derivatives [2, 3], and the antimicrobial activity of complexes of a number of transition metals with hydroxy- and carboxycoumarins [4, 5], it seemed that 3-aminocoumarin (3-AMC), which has not hitherto been examined in this context, could well be used as a ligand to obtain potentially biologically active complexes of the platinum metals. We have synthesized complex compounds of the composition $M(3\text{-AMC})_2X_2$, where M = Pt(II), X = Cl (I), Br (II), I (III); M = Pd(II), X = Cl (IV), Br (V), I (VI).

DISCUSSION OF RESULTS

A comparative analysis of the IR spectra of the complexes and the ligand 3-AMC leads us to the conclusion that the latter is coordinated to the metal via the N atom of the amino group. Evidence of this, in particular, is supplied by the shift of the bands $\nu_{as}NH_2$ and $\nu_{s}NH_2$ toward lower frequencies and by the appearance of a band due to stretching vibrations of the M–N bond at 450-470 cm^{-1} in the spectra of the complexes (Table 1). Stretching vibration of the carbonyl group of the lactone appears in the spectrum of the complexes in the form of several absorption bands, with frequencies almost the same as those of the ligand, possibly indicating that there is no coordination of the C=O group of the coumarin lactone ring with the metal. In the interval 3070-2950 cm^{-1} we observe two bands νC–H of the aromatic ring. The complexes (I) and (IV) contain water of crystallization; the IR spectrum contains an absorption band νOH at 3575-3480 cm^{-1}, disappearing on dehydration which occurs at 110-130°C without decomposition of the complexes; this is confirmed by the IR spectra and by thermography. All the synthesized complexes are stable in air; they melt with decomposition above 250°C. Treatment of compounds (I)-(III) with thiourea forms bright yellow complexes of the composition $[Pt(Thio)_4]X_2$ (X = Cl, Br, I); this is characteristic of cis isomers [9]. In each of the long-wave IR spectra of complexes (I)-(VI) we observe two absorption bands νM–X (see Table 1), typical of cis-halide compounds [8]. On examining the diffraction patterns of complexes (I)-(III) and (IV)-(VI) we see that they are isostructural;

Division of Institute of Chemical Physics, Academy of Sciences of the USSR, Chernogolovka. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2444-2447, November, 1980. Original article submitted December 20, 1979.

0568-5230/80/2911-1712$07.50

TABLE 1. Data from IR Spectra of Complexes*

Compound	νOH (water of cryst.)	νNH_2	$\nu C{=}O$	$\nu C{=}C$	δNH_2	$\nu M{-}N$	$\nu M{-}X$
3-AMC	–	3438 3320	1725 1715 1698	1600 1570	1642	–	–
(I)	3570	3250 3190	1725 1715 1700	1640 1570	1610	469	336 322
(II)	–	3210 3180	1720 1710 1690	1635 1560	1610	468	216 208
(III)	–	3200 3160	1728 1698 1682	1635 1570	1595	460	175 165
(IV)	3575 3480	3210 3190	1725 1710 1690	1630 1570	1610	459	339 305
(V)	–	3240 3160	1725 1710 1690	1630 1580	1600	458	222 219
(VI)	–	3205 3160	1725 1708 1695	1650 1590	1610	458	171 163

*Attribution of absorption bands from [6-8].

this may also serve as a confirmation of the cis structure of the Pd-complexes (IV)-(VI).

The complexes so obtained are not electrolytes, as shown by their molecular conductivities (Table 2). In solution in DMF they do not undergo chemical changes; their molecular conductivities are scarcely altered by the passage of time; and they can be precipitated from DMF solution by means of water.

A comparison between the diffraction patterns of the ligand and the complex compounds indicates that the latter are definite compounds, and the large number of diffraction maxima indicates the crystalline state of the complexes.

The derivatograms of (I)-(IV) in the interval 100-140°C display an endothermic effect due to dehydration. The numbers of molecules of water of crystallization in these compounds, determined by thermogravimetry, agree with the theoretical values. In the interval 130-240°C on the differential curve of change of temperature there is a thermal effect without loss of mass; by analogy with other diacidodiamino complexes of Pt(II) and Pd(II) [10], this can evidently be attributed to a process of isomerization of the complexes of the cis configuration to the trans form. The complexes decompose above 200°C; the endothermic effect of this process overlaps the exothermic effect of decomposition of the organic part of the molecule in the interval 200-700°C with several maxima. On the TG curve the process of decomposition corresponds to a deviation of the curve accompanied by loss of mass. In all cases the mass of the specimen reaches a constant value of 700°C, indicating the formation of the final decomposition product — the metal.

The biological activity of the complexes is being studied.

EXPERIMENTAL

The IR spectra were recorded on IK-20 and IKS-22V spectrometers with the usual method of grinding in vaseline oil and hexachlorobutadiene.

Thermal analysis was performed in a Paulik–Paulik–Erdey derivatograph. The specimens were heated to 1000°C at 10 deg/min in air. X-ray diffraction patterns were recorded in a URS-50 IM diffractometer in filtered Cu radiation. The interplanar distances were calculated with the aid of Hiller's tables. The electrical conductivity was measured in a thermostated glass cell with smooth Pt electrodes. The cell constant was determined with a standard KCl solution.

The 3-AMC was synthesized by the method in [11].

TABLE 2. Molecular Conductivities λ (in $cm^2/\Omega\cdot mole$) of Complexes of 3-AMC in DMF

Complex	C, moles/liter		
	$2\cdot10^{-3}$	$1\cdot10^{-3}$	$0{,}5\cdot10^{-3}$
(I)	9,3	11,8	15,0
(IV)	9,6	14,8	20,0

Platinum(II) cis-Dichlorobis(3-aminocoumarin), cis-$[Pt(3\text{-}AMC)_2Cl_2]H_2O$ (I). To 0.32 g (2 mmoles) of 3-AMC, dissolved in 100 ml of hot water or alcohol, was gradually added 0.34 g (1 mmole) of $K_2[PtCl_4]$ in 10 ml of water. The reaction mixture was heated on a water bath. After 10 min, a bright yellow precipitate appeared, and was filtered off, washed with alcohol and ether, and dried at 50-60°C. The yield of (I) was 80%. Complex (I) is soluble in DMF, soluble in ethylene glycol, and insoluble in water. Found: C 35.78; H 2.61; Cl 12.15; N 4.31%. $C_{18}H_{16}N_2O_5Cl_2Pt$. Calculated: C 35.66; H 2.66; Cl 11.70; N 4.68%.

Platinum(II) cis-Dibromobis(3-aminocoumarin), cis-$[Pt(3\text{-}AMC)_2Br_2]$ (II), and Platinum(II) cis-Diiodobis(3-aminocoumarin), cis$[Pt(3\text{-}AMC)_2I_2]$ (III). To a solution of 0.2 g (0.3 mmoles) of (I) in 30 ml of DMF was added 0.14 g (1.2 mmoles) of KBr or 0.2 g (1.2 mmoles) of KI in 10 ml of water. The mixture was carefully heated on a water bath at 50-60°C, and evaporated in air until a precipitate formed; this was filtered off, washed with water, alcohol, and ether, and dried at 50°C. We obtained a crystalline powder of a dark claret color, soluble in DMF, but insoluble in alcohol and water; the yield of (II) was 74%. Found: C 32.20; H 2.51; Br 23.50; N 3.93%. $C_{18}H_{14}N_2O_4Br_2Pt$. Calculated: C 31.92; H 2.08; Br 23.54; N 4.13%.

Complex (III) is a lustrous dark brown powder, soluble in DMF and alcohol but insoluble in water; the yield was 75%. Found: C 28.07; H 1.59; N 3.34%. $C_{18}H_{14}N_2O_4I_2Pt$. Calculated: C 28.03; H 1.82; N 3.61%.

Palladium(II) cis-Dichlorobis(3-aminocoumarin), cis-$[Pd(3\text{-}AMC)_2Cl_2]2H_2O$ (IV). To 0.32 g (2 mmoles) of 3-AMC in 30 ml of hot alcohol was added dropwise 0.117 g (1 mmole) of $PdCl_2$ in 10 ml of 1 N solution of HCl. Compound (IV) separated immediately in the form of a bright yellow precipitate, which was filtered off, washed with alcohol and ether, and dried. It is soluble in DMF and in ethylene glycol, but insoluble in water; the yield is 80%. Found: C 40.27; H 3.35; Cl 13.35; N 5.62%. $C_{18}H_{18}N_2O_6Cl_2Pd$. Calculated: C 40.43; H 3.38; Cl 12.23; N 5.22%.

Palladium(II) cis-Dibromobis(3-aminocoumarin), cis-$[Pd(3\text{-}AMC)_2Br_2]$ (V), and Palladium(II) cis-Diiodobis(3-aminocoumarin), cis-$[Pd(3\text{-}AMC)_2I_2]$ (VI). To a suspension of 0.21 g (0.4 mmoles) of (IV) in 100 ml of acetone was added 0.19 g (1.6 mmoles) of KBr or 0.26 g (1.6 mmoles) of KI in 10 ml of water. After standing for 1 h the initial precipitate of (IV) disappeared and the solution acquired the color of claret; the reaction mixture was then evaporated in air until a precipitate formed, and this was treated similarly to the preceding. The yield of (V) was 73%; the powder was orange. Found: C 36.62; H 2.69; Br 26.61; N 4.70%. $C_{18}H_{14}N_2O_4Br_2Pd$. Calculated: C 36.72; H 2.39; Br 27.14; N 4.75%.

Compound (VI) is a dark brown lustrous powder; yield 70%. Found: C 31.38; H 2.02; N 4.57%. $C_{18}H_{14}N_2O_4I_2Pd$. Calculated: C 31.66; H 2.06; N 4.10%. Both complexes are soluble in DMF and alcohol but insoluble in water.

Complexes (II) and (V) were also obtained by reacting $K_2[PtBr_4]$ or $K_2[PdBr_4]$ with 3-AMC in the molar ratio 1:2 in water—alcohol solution. After 3-4 days a precipitate of the complex came down; it was treated as above. Compounds (III) and (VI) could not be obtained by this method.

Kurnakov's thiourea reaction [6] for (I)-(III) was effected by the following method: 0.1 mmoles of the complex was added to 30 ml of water, and to the suspension was added an aqueous solution of 0.6 mmoles of thiourea. The precipitate disappeared and the solution became bright yellow. The solution was cooled with ice and conc. HCl added; as a result we got beautiful yellow crystals of the complexes $[Pt(Thio)_4]X_2$ (X = Cl, Br, I). Found: S 22.98%. $[Pt(Thio)_4]Cl_2$. Calculated: S 22.46%. Found: S 22.78%. $[Pt(Thio)_4]Br_2$. Calculated: S 23.38%. Found: S 19.82%. $[Pt(Thio)_4]I_2$. Calculated: S 20.21%.

CONCLUSIONS

1. The complex compounds of platinum(II) and palladium(II) with 3-aminocoumarin, with the composition $M \cdot (3\text{-AMC})_2X_2$, where M = Pt, Pd, X = Cl, Br, I, have been synthesized for the first time.

2. These complexes have the cis configuration; the ligand is coordinated with the metal via the nitrogen atom of the amino group.

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