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On the Question of the Structure of "Anomalous" Aminonitrile Complex Compounds of Divalent Platinum

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Until now there has been no single opinion regarding the structure of the "anomalous" aminonitrile compounds of divalent platinum, first discovered by L. A. Chugaev and V. V. Lebedinskii (1), and having the composition $[Pt(RCN)_2A_4]X_2$ or $[PtRCNA_4]X_2$, where RCN is a nitrile, A is an amine, and X is a monovalent anion. Divalent platinum in such compounds formally has anomalously high coordination numbers, 6 and 5, for which these compounds received the name "anomalous." V. V. Lebedinskii and V. A. Golovnya (2), on the basis of a study of the reactions of "anomalous" compounds, came to the conclusion that the "extra" amines (beyond coordination number 4 for divalent platinum) are bound not to platinum but to the nitriles, so that the coordination number of divalent platinum remains equal to 4. Developing this point of view, A. A. Grinberg and Kh. I. Gil' dengershel' (3) suggested that, upon interaction of the "extra" amines with nitriles, amidines are formed. However, Harris and Stephenson (4) interpreted the X-ray structural data they obtained for $[Pt(CH_3CN)_2(NH_3)_4]Cl_2 \cdot H_2O$ in favor of such a structure of the complex cation in which divalent platinum has coordination number 6, and 4 ammonia molecules and 2 acetonitrile molecules carry out octahedral coordination, with both acetonitrile molecules being in the trans position relative to each other and bound to platinum through the triple bonds $C \equiv N$.

To clarify the structure of the "anomalous" compounds, we studied the infrared absorption spectra (400–4000 cm^{-1}) of nitrile compounds of the type $[Pt^{II}(RCN)_2X_2]$ (where X = Cl or Br), cis-$[Pt^{IV}(RCN)_2Cl_4]$, anomalous compounds (in the form of chloroplatinite derivatives) with ammonia, methylamine, and ethylenediamine, and several complexes containing the same ligands but not "anomalous" ones*. The compounds were studied in the solid state. Pressing with potassium bromide and grinding with Vaseline oil were used.

In the spectra of the compounds $[Pt(RCN)_2X_2]$ and cis-$[Pt(RCN)_2Cl_4]$, the frequencies of the stretching vibrations of the triple bonds $C \equiv N$ appear in the region of ~ 2300 cm^{-1} (Table 1). These frequencies are increased by 50–70 cm^{-1} in comparison with the frequencies for free liquid nitriles (5). A typical

Fig. 1. IR absorption spectra in potassium bromide: a –cis-$[Pt(C_3H_7CN)_2Cl_2]$; b –$[Pt(C_3H_7CN)_2(NH_3)_4][PtCl_4]$; c –$[PtEn_2(C_3H_7CN)_2][PtCl_4]$.

Figure 1: Fig. 1. IR absorption spectra in potassium bromide: a –cis-$[Pt(C_3H_7CN)_2Cl_2]$; b –$[Pt(C_3H_7CN)_2(NH_3)_4][PtCl_4]$; c –$[PtEn_2(C_3H_7CN)_2][PtCl_4]$.

spectrum is shown in Fig. 1. The increase in $\nu(C \equiv N)$ indicates coordination of the nitriles not through the triple bond $C \equiv N$, but through the lone electron pair of the nitrogen atom, since in coordination through the triple bond one should expect a lowering of $\nu(C \equiv N)$ because of some weakening of the $C \equiv N$ bonds as a result of withdrawal of the electron cloud from these bonds toward the platinum atom. Such a lowering of frequencies was observed when molecules were coordinated through multiple bonds $C = C$ (^{6}), $C = C$ (^{7}-^{9}). Taking into account the analogous increase in $\nu(C \equiv N)$ upon formation of bonds $R - C \equiv N \rightarrow M$, where M is a complex-forming–

* A detailed description of the spectra will be presented subsequently.

forming atom, in other nitrile complexes ($^{10-13}$), it seems possible to us to conclude that withdrawal of the unshared electron pair from the nitrogen atom of nitriles leads to some strengthening of the $C \equiv N$ bonds, i.e., the unshared electron pair of the nitrogen atom has a loosening effect on the $C \equiv N$ bond.

In deciding the question of whether the "anomalous" complexes contain amidines and amines, i.e., correspond to the formula

$$\{Pt\{RC(=NH)NHR'\}_2(R'NH_2)_2\}[PtCl_4], \qquad (I)$$

or whether they contain nitriles and amines, i.e., correspond to the formula

$$[Pt(RCN)_2(R'NH_2)_4][PtCl_4], \qquad (II)$$

where $R' = H$ or a hydrocarbon radical, we proceeded from the premise that the spectra of the complexes, depending on structure I or II, should possess the following

Fig. 1. IR absorption spectra in potassium bromide:
a –cis-$[Pt(C_3H_7CN)_2Cl_2]$;
b –$[Pt(C_3H_7CN)_2(NH_3)_4][PtCl_4]$;
c –$[PtEn_2(C_3H_7CN)_2][PtCl_4]$.

features. In the spectra of compounds I there should be present, and in the spectra of compounds II absent, absorption bands near 3300–3500 cm^{-1} ($\nu(NH)$) of uncoordinated groups $-NH_2$ or $= NH$ (^{14,15}) and 1600 cm^{-1} ($\nu(C = N)$(^{14})). Conversely, in the spectra of compounds I there should be absent, and in the spectra of compounds II present, absorption bands attributable to $\nu(C \equiv N)$ of coordinated nitriles. In the spectra obtained by us for the "anomalous" complexes (typical spectra are given in Fig. 1, *b*, *c*) there are no absorption bands that could be assigned to $\nu(\mathrm{C} \equiv \mathrm{N})$. In the region ~ 3400 cm^{-1} there are absorption bands which should be assigned to ν(NH) of uncoordinated NH or NH_2 groups, since the absorption bands of coordinated groups usually lie in the region < 3300 cm^{-1}. In the spectra of all the "anomalous" complexes an intense doublet is found near 1600 cm^{-1}, the high-frequency component of which changes little in position and intensity upon deuteration at the N–H bonds and therefore must be assigned to $\nu(\mathrm{C} = \mathrm{N})$. In full agreement with this assignment, the value of $\nu(\mathrm{C} = \mathrm{N})$ for the deuterated "anomalous" butyronitrile complex with ammonia (1613–1615 cm^{-1}) lies between the value found, 1640 cm^{-1}, for the group $\mathrm{C} = \mathrm{N} - \mathrm{H}$

and the calculated value 1592 cm^{-1} for the hypothetical group

$\mathrm{C} = (\mathrm{ND})$. The low-frequency component of the doublet disappears upon deuteration and therefore must be assigned to deformation vibrations of the N–H bonds.

Thus, it may be regarded as proven that the "anomalous" compounds do indeed contain amidines and correspond to formula I. The presence of an intense doublet in the region of ~ 1600 cm^{-1} is the most characteristic indication of the presence of unsubstituted or *N*-alkylmonosubstituted amidines in the complexes.

Although we have not found direct proof as to through which group ($=\mathrm{NH}$ or $-\mathrm{NHR}'$) the amidines are bound to platinum, a number of arguments nevertheless support coordination through the $=\mathrm{NH}$ groups. It is known ([14,15]) that absorption bands belonging to ν(NH) of uncoordinated $\mathrm{C} = \mathrm{NH}$ groups lie in the region 3200-3400 cm^{-1}. In the spectra of "anomalous" compounds with En of the type $[\mathrm{PtEnRC}(=\mathrm{NH})\mathrm{NH}(\mathrm{CH}_2)_2\mathrm{NHC}(=\mathrm{NH})\mathrm{R}][\mathrm{PtCl}_4]$, the ν(NH) frequencies of uncoordinated groups are identified at 3430–

Table 1

Wave numbers of absorption-band maxima, cm^{-1} (sh –shoulder)

Compound	ν(NH)	$\nu(\mathrm{C} \equiv \mathrm{N})$	$\nu(\mathrm{C} = \mathrm{N})$
cis-$[\mathrm{Pt}(\mathrm{CH}_3\mathrm{CN})_2\mathrm{Cl}_2]$	–	2300, 2314 sh.	–
cis-$[\mathrm{Pt}(\mathrm{CH}_3\mathrm{CN})_2\mathrm{Br}_2]$	–	2314	–
trans-$[\mathrm{Pt}(\mathrm{CH}_3\mathrm{CN})_2\mathrm{Cl}_2]$	–	2307	–
cis-$[\mathrm{Pt}(\mathrm{C}_2\mathrm{H}_5\mathrm{CN})_2\mathrm{Cl}_2]$	–	2303	–
cis-$[\mathrm{Pt}(\mathrm{C}_2\mathrm{H}_5\mathrm{CN})_2\mathrm{Br}_2]$	–	2305	–

Compound	ν(NH)	$\nu(C \equiv N)$	$\nu(C = N)$
cis-$[Pt(C_3H_7CN)_2Cl_2]$	–	2311	–
cis-$[Pt(C_3H_7CN)_2Br_2]$	–	2305	–
cis-$[Pt(C_4H_9CN)_2Cl_2]$	–	2305	–
cis-$[Pt(C_6H_5CN)_2Cl_2]$	–	2280	–
$[Pt(C_2H_5CN)_2Cl_4]$	–	2319	–
$[Pt(C_3H_7CN)_2Cl_4]$	–	2312	–
$[Pt(C_4H_9CN)_2Cl_4]$	–	2319	–
$[Pt(C_6H_5CN)_2Cl_4]$	–	2288	–
$[Pt(CH_3CN)_2(NH_3)_4][PtCl_4]$, pink	~ 3170 sh., ~ 3290, 3412	–	1638
$[Pt(CH_3CN)_2(NH_3)_4][PtCl_4]$, green	~ 3237 sh., ~ 3300, 3409	–	1635
$[Pt(C_3H_7CN)_2(NH_3)_4][PtCl_4]$	several bands at ~ 3230–3430	–	1640
$[Pt(C_6H_5CN)_2(NH_3)_4][PtCl_4]$	3040–3240	–	1629
cis-$[Pt(C_2H_5CN)NH_3Cl_2]$	3117?, 3211, 3289	2302	–
$[Pt(CH_3CN)_2En_2][PtCl_4]$ H_2O	~ 3175, ~ 3440	–	1617
$[Pt(C_2H_5CN)_2En_2][PtCl_4]$ H_2O	3126, 3236, ~ 3450	–	1607
$[Pt(C_3H_7CN)_2En_2][PtCl_4]$	3126, ~ 3238, ~ 3470 sh.	–	1602
$[Pt(C_4H_9CN)_2En_2][PtCl_4]$	3126, ~ 3241, ~ 3430 sh.	–	1605
$[Pt(CH_3CN)_2En_3][PtCl_4]$	~ 3120, 3213, 3279, ~ 3470	–	1625
$[PtEn_2]Cl_2$	3063, 3146	–	–
$[Pt(CH_3CN)_2(CH_3NH_2)_4][PtCl_4]$	3136, 3221, 3298, 3354	–	1617
$[Pt(C_2H_5CN)_2(CH_3NH_2)_4][PtCl_4]$	3131, ~ 3220, 3287, ~ 3460 sh.	–	1625
cis-$[Pt(CH_3NH_2)_2Cl_2]$	3129, 3226, 3271	–	–

3470 cm^{-1}, i.e., in the region > 3400 cm^{-1}. Therefore they apparently do not belong to ν(NH) of uncoordinated $C = NH$ groups. In other words, the $C = NH$ groups apparently are not free, but are bound to platinum. Further, using the Bellamy–Williams relation (16) for the frequencies of symmetric and antisymmetric valence vibrations of uncoordinated amino groups,

$$\nu_s = 345.5 + 0.876\,\nu_{as}\ \text{cm}^{-1},$$

it can be shown that in the "anomalous" complexes with ammonia the amino group is apparently uncoordinated. In the spectrum of

$$[\text{Pt}(\text{C}_3\text{H}_7\text{CN})_2(\text{NH}_3)_4][\text{PtCl}_4], \tag{III}$$

partially deuterated in order to lower the intensity of the bands belonging to ν(NH), the ν(NH) frequencies 3429, 3395, 3359, and 3310 were identified; these may be assigned to uncoordinated NH_2 or NH groups (> 3300 cm^{-1}). If the first two frequencies are assigned to $\nu_{as}(NH_2)$ (the appearance of two frequencies can be explained by the presence of two groups or by resonance splitting), then the values of $\nu_s(NH_2)$ calculated according to the Bellamy-Williams relation, equal to 3349 and 3320 cm^{-1}, agree well with the observed values 3359 and 3310 cm^{-1}. The somewhat increased difference, ±10 cm^{-1}, between the calculated and observed values, in comparison with the usual one (4.8 cm^{-1} for amine solutions), is not unexpected, since the error of our measurements in this region may reach ±4–5 cm^{-1}. In addition, small deviations from the Bellamy-Williams relation for the solid state are not excluded because of stronger intermolecular interactions. Thus, the applicability of the Bellamy-Williams relation to complex III indicates that in III the amino groups are uncoordinated, i.e., coordination takes place through the $=$ NH groups.

We believe that in the formation of amidines there is no rupture of the platinum –nitrile nitrogen bond, as proposed in (^{17}), but that the amine reacts with the nitrile in the inner sphere of the complex. This proposal is consistent with coordination of the amidine through the $= \text{N} - \text{H}$ groups and the formation of cis complexes. The cis configuration of the complexes was shown earlier by cleavage with acids of the "anomalous" ammonianitrile compounds.

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