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INTERMOLECULAR INTERACTIONS IN TETRAKIS(ARYLISONITRILE)-PLATINUM(II) TETRACYANOPLATINATE(II)

H.J. KELLER* and R. LORENTZ

Anorganisch-Chemisches Institut der Universität Heidelberg, 6900 Heidelberg 1 (B.R.D.)

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Summary

A new reaction allows the preparation of complexes of the general formulae $[Pt(CNR)_4][Pt(CN)_4]$ and $[Pt(CNR)_2(CNR')_2][Pt(CN)_4]$. The compounds are characterized by their analyses and infrared spectra; their colours range from orange to dark blue indicating strong interionic interactions. The complexes are soluble in concentrated sulfuric acid and are regained without decomposition by adding water

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Results and discussion

In recent years we have been working on the preparation and investigation of metal complexes crystallizing in so-called columnar structures with intermolecular interactions in the solid state [1]. In this context we have found now a whole series of new isonitrileplatinum compounds of the general formula $[Pt(CNR)_4][Pt(CN)_4]$ [2]. They all exhibit a strong absorption in the visible part of the spectrum which we believe is due to relatively strong intermolecular or even intermetallic interactions of the participating ions of the compounds. A few examples of the group with aliphatic isonitriles [R = t-butyl, ethyl, methyl] have been presented recently. The solids were prepared by mixing solutions each containing one of the product-forming complex ions [3]. Our compounds, containing mainly aromatic isonitriles, show very similar physical characteristics but the interionic interactions seem to be improved. The method of preparation is different from that already described: A solution of *cis*-dichlorobis(isonitrile)platinum(II) in chloroform is added to a solution of isonitrile and sodium tetracyanoplatinate(II) in ethanol, effecting formation of tetrakis(isonitrile)platinum(II) tetracyanoplatinate(II):

$$PtCl_2(CNR)_2 + Na_2Pt(CN)_4 + 2RNC \xrightarrow{CHCl_3/EtOH} [Pt(CNR)_4][Pt(CN)_4] + 2NaCl$$

In a very similar reaction involving a different isonitrile (R'NC) in the starting

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR COMPLEXES $[Pt(CNR)_4][Pt(CN)_4]$

Compound	R	Colour	Analysis, found (calcd.) (%)			IR data (cm^{-1})	
			C	H	N	$\nu(C{\equiv}NR)$	$\nu(C{\equiv}N)$
I	Phenyl	Dark blue	42.19 (42.4)	2.46 (2.2)	12.22 (12.4)	2260, 2220	2140
II	4-Ethylphenyl	Blue	46.86 (47.15)	3.81 (3.5)	10.77 (11.0)	2270, 2250, 2225	2140
III	2,6-Dimethylphenyl	Purple	46.65 (47.15)	3.88 (3.5)	10.94 (11.0)	2240, 2215(sh)	2140
IV	4-Methoxyphenyl	Orange	41.93 (42.1)	3.28 (2.73)	10.69 (10.9)	2230(br)	2137
V	Cyclohexyl	Violet	41.21 (41.3)	4.97 (4.7)	11.88 (12.0)	2287, 2260, 2240	2135

complex a "mixed" compound may be obtained, i.e. $[Pt(CNR)_2(CNR')_2][Pt(CN)_4]$.

It is important to follow the given instructions of preparation in order to get analytically pure complexes because if the sequence of mixing is altered only impure material is obtained.

In the way described we have prepared the compounds of stoichiometry $[Pt(CNR)_4][Pt(CN)_4]$ and $[Pt(CNR)_2(CNR')_2][Pt(CN)_4] \cdot xH_2O$ listed in Tables 1 and 2. They are highly insoluble in common solvents, except complex IV,

TABLE 2

PHYSICAL AND ANALYTICAL DATA FOR COMPLEXES $[Pt(CNR)_2(CNR')_2][Pt(CN)_4] \cdot xH_2O$

Compound	R, R'		Colour	Analysis, found (calcd.) (%)			IR data (cm^{-1})	
				C	H	N	$\nu(C{\equiv}NR)$	$\nu(C{\equiv}N)$
VI	Phenyl, 4-ethylphenyl	$x=0$	Blueviolet, copperlustre	45.23 (44.90)	3.38 (2.90)	11.60 (11.70)	2265, 2245(sh), 2225	2140
VII	Phenyl, 2,6-dimethylphenyl	$x=1$	Dark brown violet	44.15 (44.10)	3.31 (3.10)	11.28 (11.40)	2250, 2220(sh)	2140
VIII	Phenyl, 2,6-diethylphenyl	$x=1$	Dark red violet	46.31 (46.40)	3.62 (3.70)	10.77 (10.80)	2255, 2220(sh)	2140
IX	Phenyl, azobenzene-4	$x=1$	Blueblack	46.62 (46.40)	2.97 (2.65)	14.87 (14.85)	2260, 2225	2140
X	Phenyl, tert-butyl	$x=2$	Violet, copperlustre	37.17 (37.30)	3.38 (3.54)	12.31 (12.40)	2305(sh), 2270, 2230(sh), 2200(sh)	2140
XI	Cyclohexyl, phenyl	$x=1$	Violet, copperlustre	41.05 (41.00)	3.75 (3.70)	11.98 (11.95)	2265, 2245, 2228	2140
XII	Cyclohexyl, 2,6-dimethylphenyl	$x=2$	Violet, blackgreenlustre	42.81 (42.80)	4.49 (4.36)	11.13 (11.10)	2280, 2250	2140
XIII	Cyclohexyl, tert-butyl	$x=1$	Red violet, green goldlustre	37.30 (37.50)	4.68 (4.70)	12.74 (12.50)	2282, 2260(sh) 2250	2138

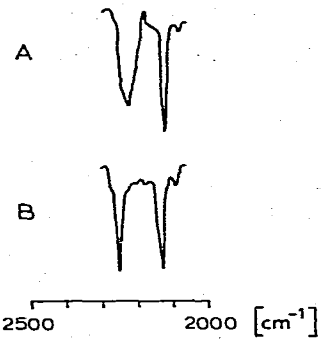

Fig. 1. IR spectrum of complex IV; A, in the solid state (Nujol Mull); B, in EtOH solution.

where a considerable solubility is observed in ethanol. The colour of this latter solution varies from dark red (concentrated) to yellow (diluted), a fact which in our opinion suggests a reversible association with interactions of the ions already in the solution.

Very surprisingly we found that the complexes are soluble in concentrated sulfuric acid. They dissolve to give a nearly colourless, slightly yellow solution and — by adding water — can be reprecipitated without decomposition as the same deeply coloured solid! This reaction is quite embarrassing as the acid solvent does not seem to attack the isonitrile whereas the uncoordinated ligand is destroyed very rapidly by the action of the acid. As demonstrated by their identical IR spectra and the analysis of the reprecipitated complex VI (calculated for a unit containing 1 H_2O) (found: C, 44.24; H, 3.25; N, 11.08; S, 0.07. $C_{36}H_{30}N_8OPt_2$ calcd.: C, 44.08; H, 3.06; N, 11.43; S, 0%) the material is recovered unchanged after treatment with concentrated sulfuric acid.

The infrared spectra of all the complexes $[Pt(CNR)_4][Pt(CN)_4]$ exhibit the same pattern. The $\nu(C{\equiv}NR)$ of the isonitrile in the cation is split while the $\nu(C{\equiv}N)$ of the anion is a single sharp absorption. The splitting of the isonitrile C≡N-stretching mode (a single absorption is required according to the selection rules of IR spectroscopy [4]) seems to be caused by distortions or other symmetry-lowering effects in the solid state. In fact, the IR absorption spectrum of complex IV in ethanol is markedly different from the spectrum of the same compound as a solid in nujol (Fig. 1). In solution two unsplit bands of equal intensity for $\nu(C{\equiv}N)$ and $\nu(C{\equiv}NR)$ are observed, in full agreement with the selection rules mentioned above. As expected, all of the $\nu(C{\equiv}NR)$ frequencies of the free isonitriles are shifted to shorter wavelengths upon complexation.

Experimental

1. Isonitriles RNC: XIV, R = phenyl; XV, 4-ethylphenyl; XVI, 4-methoxyphenyl; XVII, 4-azobenzene

Preparation analogous to those described in the literature [5] (additional heating in case of XVII); purification by distillation (XIV, XVI) or chromatography on silica gel (0.05-0.2) in benzene (XV, XVII)*.

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* Cyclohexylisonitrile, 2,6-dimethylphenylisonitrile, 2,6-diethylphenylisonitrile and t-butylisonitrile were donated by Bayer Leverkusen. We would like to thank Prof. Kurt Ley for his generosity.

2. Complexes $PtCl_2(CNR)_2$

Complexes $PtCl_2(CNR)_2$ (R = phenyl, cyclohexyl) are prepared according to the literature [6].

3. Complexes I-XIII

$Na_2Pt(CN)_4$ (0.1 g) is dissolved in about 20 ml of ethanol and the appropriate amount of isonitrile (RNC or R'NC) is added. This is added to a stoichiometric solution of $PtCl_2(CNR)_2$ in chloroform (20-50 ml).

Complex IV is recovered by adding petroleum ether 100/140 and concentrating (ethanol and chloroform are evaporated under reduced pressure). The orange precipitate is filtered off and washed with petroleum ether, small amounts of ethanol and water, and dried in high vacuum.

All the other complexes I-III, V-XIII precipitate immediately upon mixing the two reacting solutions. The microcrystalline products are filtered and washed with ethanol and water and dried in high vacuum. In case of I these operations were accomplished with a centrifuge as the very fine particles were not retained by the filter.

IR measurements were carried out on a 221 model Perkin—Elmer and a Unicam SP 1000 of Pye—Unicam.

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