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Solid Bis(1,10-phenanthroline)platinum(II)- and Bis(2,2′-bipyridyl) platinum(II) Platinates(II) with Intermolecular Metal–Metal Interactions

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Introduction

Little's recent theoretical proposal of a possible model compound for a high temperature superconductor requires a platinum(II) complex with neutral cyanine dye base type ligands[1]. This proposal is a very much more precisely defined system than the basic exciton model proposed several years earlier[2], and holds much more promise of being capable of synthesis. The cationic species would consist of a central d^8 Pt(II) which is in direct contact with *four* dyes (Figure 1) (earlier Winkler and Mayer achieved mono dye substituted complexes of Ir(I) and Pt(II)[3]). The platinum dye units are required to be incorporated in a so-called columnar structure[4] in the crystal, *i.e.* an arrangement of these square planar complexes one on top of the other, the metal atoms of which provide the conductive "spine". Further, it is important that strong Pt–Pt interactions should prevail in this stack, so as to obtain a material with an one-dimensional, highly-conducting spine surrounded by an easily polarized environment which provides the attractive interaction necessary for superconductivity.

As little is known about bis(1,10-phenanthroline) Pt(II) complexes even without such sophisticated substituents[5], we undertook the synthesis of several new types of complex compounds all containing the cation $[PtL_2]^{2+}$, which we report here. L may represent 1,10-phenanthroline or 4,7-dimethyl-1,10-phenanthroline. As the 2,2′-bipyridyl system is closely related to the 1,10-phenanthroline ligand we also introduced for L the 2,2′-bipyridyl[6,7] and 5,5-dimethyl-2,2′-bipyridyl donors.

Experimental

The following abbreviations are used for the N-heterocyclic ligands: L^1: 2,2′-bipyridyl: $C_{10}H_8N_2$; L^2: 5,5′-dimethyl-2,2′-bipyridyl: $C_{12}H_{12}N_2$; L^3: 1,10-phenanthroline: $C_{12}H_8N_2$; L^4: 4,7-dimethyl-1,10-phenanthroline: $C_{14}H_{12}N_2$; L: L^1, L^2, L^3 or L^4.

Chemicals

$PtLCl_2$ is obtained as described earlier[8]. $[PtL_2]Cl_2$ is prepared in solution in the same way as described for L^1 = 2,2′-bipyridyl[6]. An aqueous suspension of $PtLCl_2$ is heated with excess of free ligand L until a clear yellow solution results containing $[PtL_2]Cl_2$ and some free L (in case of L^4 a $H_2O/EtOH = 1:2$ mixture is used instead of water).

Bis(1,10-phenanthroline)platinum(II) diiodide (II)

A solution of $[PtL^3{}_2]Cl_2$ is treated with a five-fold excess of KI (aqueous solution). The resulting yellow precipitate is filtered off, and is carefully recrystallized in water (50–60° C) to yield small orange needles. Analytical data of the product $[Pt(C_{12}H_8N_2)_2]I_2$: found: 35.45%C, 2.05%H, 6.80%N, 31.67%I, 24.1%Pt; calc.: 35.60%C, 2.00%H, 6.42%N, 31.40%I, 24.1%Pt.

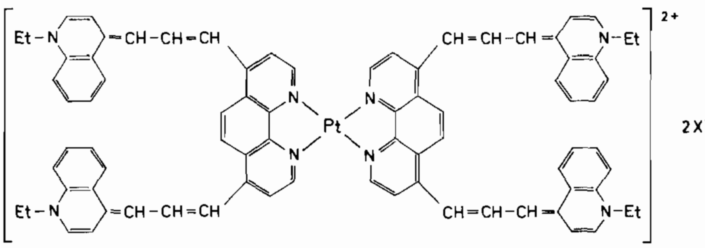

Figure 1. Proposed model of high-temperature superconductor.

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Reactions of $[PtL_2]Cl_2$ with $K_2[PtZ_4]$ ($Z = Cl^-$, CN^-, NO_2^-, $1/2C_2O_4^{2-}$) (III–XIV)

The products $[PtL_2][PtZ_4]$ consist of microscopic particles which tend to stick together during filtration thus preventing an efficient subsequent purification. The following two methods proved to be successful in removing KCl and free ligand L from the product.

(i) A filtered aqueous solution of 200 mg K_2PtZ_4 is prepared and combined with stoichiometric amounts of a filtered solution of $[PtL_2]Cl_2$. The resulting precipitate is allowed to settle, the solvent is decanted, and water is added. The procedure of sedimentation and decanting of water is repeated several times to remove KCl. In order to remove free L the product is treated in the same way with enthanol. Finally the pure complex compound is filtered and dried under high vacuum.

(ii) A $[PtL_2]Cl_2$ solution is filtered into a boiling, filtered aqueous K_2PtZ_4 solution. The reaction mixture is kept at 100° C, is filtered while hot and the product is washed with boiling water. Care must be taken that the water is kept hot enough to dissolve L. The compound again is dried under high vacuum.

$[PtL^3_2][PtCl_4]$ (IX) is also obtained in the reaction of 1,10-phenanthroline with K_2PtCl_4 (similar to $[PtL^1_2][PtCl_4]$[6].

For the analytical data of the complexes with stoichiometry $[PtL_2][PtZ_4]$ see Table I.

Preparation of $[Ptpy_4][Pt(CN)_4]$ (py = pyridine) (XV)

Stoichiometric amounts of $[Ptpy_4]Cl_2$[9] solution and aqueous $K_2Pt(CN)_4$ yield a colorless precipitate which is recrystallized in hot water. Analytical data for $[Pt(C_5H_5N)_4][Pt(CN)_4]$: found: 35.44%C, 2.67%H, 13.89%N, 48.35%Pt; calc: 35.55%C, 2.47%H, 13.83%N, 48.15%Pt.

Results and Discussion

$[PtL^3_2]X_2$ ($X = Cl,I$) (I, II)

A synthesis of the bis-phenanthroline or bis-bipyridyl substituted Pt(II) cationic species $[PtL_2]^{2+}$ is achieved by starting with the mono-substituted $PtLCl_2$ which is easily prepared from L and K_2PtCl_4 in acid solution. An aqueous suspension of $PtLCl_2$ reacts while hot with excess of L to form a light yellow solution containing $[PtL_2]^{2+}$.

$$PtLCl_2 + L \xrightleftharpoons{H_2O} [PtL_2]^{2+} + 2Cl^- \qquad (1)$$

Reaction (1) had already been run earlier with L = L^1 = 2,2′-bipyridyl; a separation of the product, however, was not possible as $[PtL^1_2]Cl_2$ decomposed upon concentrating[6, 7].

TABLE I. Analytical Data for Complexes $[PtL_2][PtZ_4]\cdot xH_2O$ [found (calc.)].

	L	Z	x	%C	%H	%N	%Pt
III	L^1=2,2′-bipyridyl	CN	0	35.69 (35.73)	1.99 (1.99)	13.81 (13.90)	47.9 (48.39)
IV		$1/2(C_2O_4)$	1/2	32.57 (32.47)	1.78 (1.91)	6.39 (6.31)	43.6 (43.96)
V		NO_2	0	27.26 (27.09)	1.87 (1.81)	12.31 (12.64)	43.9 (44.02)
VI	L^2=5,5′-dimethyl-2,2′-bipyridyl	CN	1 1/2	37.61 (37.80)	2.80 (3.03)	12.45 (12.60)	43.75 (43.86)
VII		$1/2(C_2O_4)$	1	35.25 (35.29)	2.83 (2.73)	5.94 (5.88)	40.42 (40.96)
VIII		NO_2	0	30.61 (30.57)	2.54 (2.57)	11.66 (11.88)	41.33 (41.41)
IX	L^3=1,10-phenanthroline	Cl	0	32.41 (32.29)	1.73 (1.80)	6.41 (6.28)	
X		CN	1	38.84 (38.53)	2.28 (2.06)	12.91 (12.84)	44.59 (44.73)
XI		$1/2(C_2O_4)$	1/2	36.14 (35.94)	2.07 (1.81)	6.04 (5.98)	41.63 (41.71)
XII		NO_2	0	30.94 (30.84)	1.82 (1.71)	11.72 (11.99)	41.70 (41.76)
XIII	L^4=4,7-dimethyl-1,10-phenanthroline	$1/2(C_2O_4)$	1	38.14 (38.40)	2.56 (2.60)	5.79 (5.60)	38.79 (39.00)
XIV		NO_2	0	34.15 (33.94)	2.44 (2.42)	11.12 (11.31)	

Performing the same operations with L = L^3 = 1,10-phenanthroline we observe a greater stability of $[PtL^3_2]Cl_2$ and can isolate a microcrystalline, light yellow solid (I) from the reaction mixture by evaporating the water. This material is soluble in water and can be recrystallized from ethanol. The analysis of I is 51.69%C, 3.37%H, 10.06%N, 18.52%Pt, corresponding to an atomic ratio of Pt:C:N = 1:45.3:7.6. This suggests a formulation of a complex which still contains excess of free ligand and water, *i.e.* $[PtL^3_2]Cl_2 \cdot 1.75\,L^3 \cdot 6H_2O$ (calc.: $C_{45}H_{42}N_{7.5}Pt_1Cl_2$: 51.48%C, 4.00%H, 10.01%N, 18.59%Pt). $[PtL^3_2]I_2$ is obtained by adding KI to $[PtL^3_2]Cl_2$ solutions thus precipitating the less soluble, yellow complex (II) (similar to the bipyridyl compound $[PtL^1_2]I_2$ described earlier[6]). This phenanthroline analogue can be recrystallized carefully from water yielding small orange needles of $[Pt(C_{12}H_8N_2)_2]I_2$. A further color change as has been observed with $[PtL^1_2]I_2$ (red to black)[6, 10] does not occur.

$[PtL^3_2][PtCl_4]$ *(IX)*

The tetrachloroplatinate salt of $[PtL_2]^{2+}$ is prepared easily by direct combination of L and K_2PtCl_4:

$$2\,K_2PtCl_4 + 2\,L \rightarrow [PtL_2][PtCl_4] + 4\,KCl \qquad (2)$$

In this way the 2,2′-bipyridyl complex has already been prepared as a yellow solid[6]. By taking L = L^3 = 1,10-phenanthroline instead of L^1 again a yellow complex, $[PtL^3_2][PtCl_4]$ (IX), is precipitated. Additionally IX may also be prepared according to (3) as shown below.

$[PtL_2][PtZ_4]$ $(L = L, L^3,\quad Z = CN^-,\quad 1/2(C_2O_4)^{2-})$ *(III, IV, X, XI)*

Precipitation of $[PtL_2]^{2+}$ with Pt(II) complex anions $[Pt(CN)_4]^{2-}$ and $[Pt(C_2O_4)_2]^{2-}$ yield some new and interesting compounds:

$$[PtL_2]^{2+} + 2Cl^- + K_2PtZ_4 \xrightarrow{H_2O} [PtL_2][PtZ_4] + 2KCl \qquad (3)$$

Although the products of (3) are all microcrystalline solids with no apparent solubility in common solvents they are most exciting because of their unusual colors. Some of them appear red, violet, or even blue violet, especially if L = L^1, L^3 (III, IV, X, XI). These colors cannot arise from the yellow cation and the light yellow or colorless anion alone. Therefore we suggest that the complexes crystallize in columnar stacks resulting in relatively strong intermolecular interactions in the solid state to cause absorption in the visible part of the spectrum. Such behaviour is known in various other kinds of Pt(II) coordination compounds, *e.g.* the blue $Pt(dmg)_2$ (dmg = dimethylglyoxime), the ionic Magnus Green Salt $[Pt(NH_3)_4][PtCl_4]$[4], or in the whole group of isonitrile complexes $[Pt(CNR)_4][PtZ_4]$ (Z = Cl, CN) with colors ranging from yellow to dark blue[11].

The colors of the most interesting $[PtL_2][PtZ_4]$ compounds (III, IV, X, XI) depend to some extent on the water which they contain. $[PtL^3_2][Pt(C_2O_4)_2]$ (XI) appears after preparation in H_2O as a violet material changing to blue–violet upon desiccation. The dried, blue-shaded complex is found with 0.5 H_2O per unit, but as it is very hygroscopic it reabsorbs water on exposure to air. The analysis then indicates about 2.5 H_2O and the appearance again is violet. Shifts of the other complexes during drying are: $[PtL^3_2][Pt(CN)_4]$ (X) red to red violet, $[PtL^1_2][Pt(CN)_4]$ (III) orange to red, $[PtL^1_2][Pt(C_2O_4)_2]$ (IV) red violet to orange. These last three compounds, however, are not as hygroscopic as XI and so remain unchanged in the air after being dried. It is remarkable that the absorption maximum is shifted to longer wavelengths in case of III, X, XI by removing the water while the opposite is found with IV. A definite explanation of this phenomenon of course cannot be given without X-ray analysis but one may conclude that water presumably forms hydrogen bonds to the anions, $Pt(CN)_4{}^{2-}$ and $Pt(C_2O_4)_2{}^{2-}$ and so by electronic or steric influence partially determines the degree of intermolecular interaction in the solid state.

In order to determine the exact solid state absorption of $[PtL_2][PtZ_4]$ in the visible the complexes were mixed with KBr, powdered, and pressed into thin transparent pellets. These were mounted in a UV spectrometer (Beckmann DK-2) and the absorption spectrum was recorded over the range of 350 to 700 nm. A characteristic of all these spectra is an increasing absorption towards shorter wavelengths approaching 450 nm–presumably caused by the ions themselves. Additionally we find with III, IV, X, XI, distinct separate absorption peaks at longer wavelengths (see Figure 2). The absorption maxima λ[nm] can easily be determined and are listed in Table II.

Another convenient method of measuring λ is by taking the reaction mixture of (3), diluting it with water, and then taking an absorption spectrum of the suspension. This is only possible because the particle size of $[PtL_2][PtZ_4]$ is so extremely small that a suspension appears like a true *solution* of dye. The spectra resemble very much those described above but the absorption maxima are of course different as they now represent the "hydrated" forms of the complexes.

As it proved to be nearly impossible to obtain good suspensions of the filtered and dried complexes in a non-aqueous solvent the following procedure was introduced. Reaction mixture (3) was allowed to settle, the supernatant H_2O was decanted. Ethanol was added and was again decanted after settling of the product. Then more ethanol and benzene was added, the mixture was boiled and the last traces of water were so removed in the azeotropic mixture. The resulting suspension of the dried compound could now be

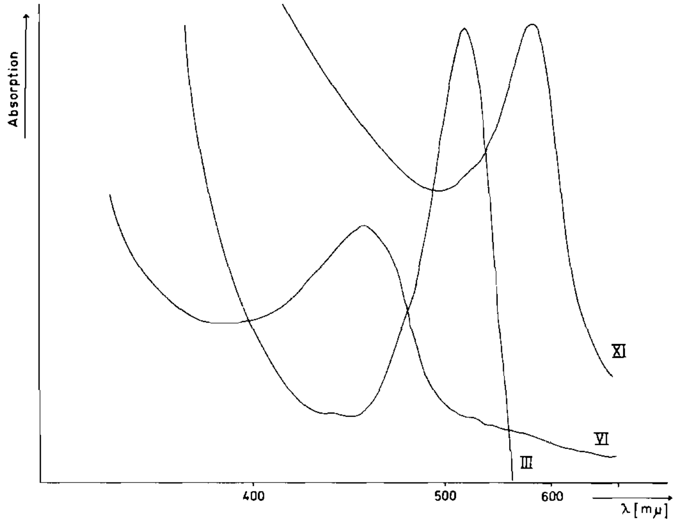

Figure 2. Absorption spectra in the visible of III) $[PtL^1_2][Pt(CN)_4]$ in KBr pellet, VI) $[PtL^2_2][Pt(CN)_4]$ in H_2O suspension, XI) $[PtL^3_2][Pt(C_2O_4)_2]$ in ethanol/benzene suspension.

TABLE II. Colors and Absorption Maxima λ (nm) of Complexes $[PtL_2][PtZ_4]$.

	L	Z	KBR Pellet		Aqueous Suspens.		Ethanol–Benzene Susp.	
			Color	λ [nm]	Color	λ [nm]	Color	λ [nm]
III	L^1=2,2′-bipyridyl	CN	red	514	orange	485	red	515
IV		$1/2(C_2O_4)$	orange	~480sh	red violet	555	orange	495
V		NO_2	light yellow	~390				
VI	L^2=5,5′-dimethyl-	CN	yellow	440sh	yellow	450		
VII	2,2′-bipyridyl	$1/2(C_2O_4)$	yellow	–	yellow	–		
VIII		NO_2	light yellow	–	light yellow	–		
X	L^3=1,10-phenanthroline	CN	red violet	550	red	532	red violet	545
XI		$1/2(C_2O_4)$	red violet	537	red violet	540	blue violet	575
XII		NO_2	yellow	410sh				
XVI	L^4=4,7-dimethyl-	CN	light yellow	~382				
XIII	1,10-phenanthroline	$1/2(C_2O_4)$	light yellow	~390 weak				
XIV		NO_2	light yellow	~385				

used for measurement and the quality of the absorption spectra was as good as usual.

The reason why this last method was developed is that it proved helpful in determining the exact absorption maximum of the dried blue violet complex $[PtL^3_2]$ $[Pt(C_2O_4)_2]$ (XI) which was found to be 575 nm. Especially because in that case the KBr method failed because during preparation of the pellet the hygroscopic complex always attracted much water. So while recording the spectrum enough water was absorbed to shift the absorption to shorter wavelengths and a value was found which was identical with that one of the aqueous suspension (Table II).

$[PtL_2][PtZ_4]$ ($L = L^2, L^4, Z = CN^-, 1/2(C_2O_4)^{2-}$) (*VI, VII, XVI, XIII*)

As soon as we introduce methyl substituted ligands, *i.e.* 5,5′-dimethylbipyridyl (L^2) and 4,7-dimethyl-1,10-phenanthroline (L^4), the intermolecular interactions of $[PtL_2][PtZ_4]$ get very much reduced. Of significance is the yellow or light yellow colors of all these compounds which do not even change upon drying. The visible spectra consist here also of an increasing absorption from 700 to 400 nm, but the additional "interaction band" is now shifted towards the u.v., *e.g.* with L^4 (XVI, XIII) some very weak absorption bands occur or only a shoulder may be seen in the ascending part of the main absorption. Only in case of the yellow $[PtL^2{}_2][Pt(CN)_4]$ (VI) a separate absorption band can be recognized at 450 nm (see Figure 1). Nevertheless it is remarkable that absolutely no "interaction band" is present with $[PtL^2{}_2][Pt(C_2O_4)_2]$ (VII) although this complex appears in the same yellow color as the cyano analogue (see Figure 3).

$[PtL^2{}_2][Pt(C_2O_4)_2]$: *Modifications*

If the complex cation with 5,5′-dimethyl-2,2′-bipyridyl ligand, $[PtL^2{}_2]^{2+}$, is precipitated by $[Pt(C_2O_4)_2]^{2-}$ at room temperature (25° C), a yellow product (VII) is obtained. If, however, the same process is performed with cooled solutions (4° C) a *red* product is formed. Upon warming a little, this color changes irreversibly to dark violet, and then finally turns, in another irreversible step, to yellow. This last modification now may be recovered as usual, and gives the same product obtained at room temperature (see Figure 3).

The red and violet materials are very unstable and even in the cold reaction mixture gradually turn yellow. An attempt to separate them immediately after preparation failed, too, as both after filtration and drying again yielded the yellow product.

The existence of both modifications can be demonstrated by recording the visible spectrum during the transitions. Initially an absorption maximum appears with λ = 525 nm corresponding to the red complex. This peak then decreases and another absorption at 580 nm turns up arising from the violet compound. The last change from violet to yellow can only be seen as a decrease of the peak at 580 nm because the final complex–as has been stated before–does not exhibit a separate absorption band.

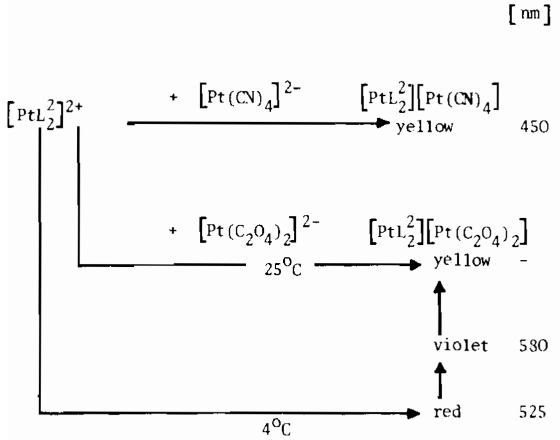

Figure 3. Precipitation products of the cation $[PtL^2{}_2]^{2+}$ (L^2 = 5,5′-dimethyl-2,2′-bipyridyl).

This behaviour now indicates for the first time that a complex with the methyl-substituted ligand L^2 may be obtained in a modification with considerable intermolecular interaction. This example really seems to be unique as all other attempts to synthesize long wavelength absorbing modifications of either $[PtL_2][Pt(C_2O_4)_2]$ or $[PtL_2][Pt(CN)_4]$ ($L = L^2, L^4$) were unsuccessful. The formation of the already found yellow complexes VI, XVI, XIII was not affected by variation of the reaction conditions such as temperature or concentration.

$[PtL_2][PtZ_4]$ *($Z = NO_2^-, SCN^-$)*

Another precipitating agent for $[PtL_2]^{2+}$ is the anionic complex salt $K_2Pt(NO_2)_4$ yielding $[PtL_2][Pt(NO_2)_4]$ (V, VIII, XII, XIV). All products absorb light of short wavelength, therefore any possible intermolecular interaction should be small. In fact the spectra of V, XII, XIV exhibit very weak additional bands in the main absorption of the two complex ions. One exception is $[PtL^2{}_2][Pt(NO_2)_4]$ (VIII) where–as with $[PtL^2{}_2][Pt(C_2O_4)_2]$ (VII)–no significant band appears (see Table II).

Some preliminary precipitation experiments with $K_2Pt(SCN)_4$ and solutions of $[PtL_2]Cl_2$ ($L = L^1, L^3$) gave two orange compounds. But as $[Pt(SCN)_4]^{2-}$ itself is of dark red and $[PtL_2]^{2+}$ of yellow appearance, an orange product is nothing unusual and we did not undertake any further preparations.

$[Ptpy_4][Pt(CN)_4]$ *(py = pyridine)*

Substituting two L in $[PtL_2][PtZ_4]$ by four pyridines also diminishes the intermolecular interactions. By treating the colorless solution of $[Ptpy_4]Cl_2$ with K_2PtCl_4 only a pink $[Ptpy_4][PtCl_4]$ is obtained[9] and by introducing $K_2Pt(CN)_4$ the resulting $[Ptpy_4][Pt(CN)_4]$ (XV) is found to be colorless. Actually XV differs very much from the other $[PtL_2][PtZ_4]$ as it is fairly highly soluble in hot water from which it may be recrystallized without decomposition.

Conclusions

If bis-bipyridyl or bis-phenanthroline substituted platinum(II) units $[PtL_2]^{2+}$ should be incorporated into a complex compound with intermolecular interactions only a combination with $[Pt(CN)_4]^{2-}$ or $[Pt(C_2O_4)_2]^{2-}$ seems promising. If substituents are introduced in the 5,5′-positions, or 4,7-positions respectively, a reduction of these interactions must be considered. However, it does not seem impossible to obtain complexes with substituted ligands and with strong interactions if there is for example a special preparation where the compound is formed just in such a suitable modification.

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