

Properties of electronic spectra of antitumor-active dichlorobis(cycloalkylamine)platinum(II) compounds

Jürgen Kritzenberger*, Hartmut Yersin**

Institut für Physikalische und Theoretische Chemie, Universität Regensburg, W-8400 Regensburg (Germany)

Manfred Zabel and Klaus-Jürgen Range**

Institut für Anorganische Chemie, Universität Regensburg, W-8400 Regensburg (Germany)

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Abstract

Complexes of $\text{PtCl}_2(\text{RNH}_2)_2$, with $\text{RNH}_2 =$ cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine and cyclooctylamine, are investigated as powder samples and in solution applying different spectroscopic methods (absorption, excitation, emission, emission lifetime). It is concluded that the involved low energy states are mainly of metal d character. All these complexes exhibit a similar spectroscopic behavior despite the strongly different properties of the $\text{PtCl}_2(\text{RNH}_2)_2$ compounds in tests against a cancer cell line. Moreover, crystallographic unit cells of the compounds are determined from powder diffraction measurements.

Introduction

More than 20 years ago, Rosenberg *et al.* observed that *cis*-diamminedichloroplatinum(II) (cisplatin) caused inhibition of cell division and induced anomalous growth of *Escherichia coli* cells [1, 2]. Subsequently, the potential value of this and other platinum compounds was documented in a large number of investigations in the field of cancer chemotherapy (e.g. see reviews in refs. 3 and 4). In particular, dichloroplatinum(II) complexes with two amines as ligands were used as potential antitumor drugs [5].

We tested a series of *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes against the human MDA-MB-231 breast cancer cell line as a tumor model. The following cycloalkylamines were used: cyclopropylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, cycloheptylamine, cyclooctylamine (Table 1). The antitumor effect of these compounds depends on the size of the cycloalkyl ring. This is most obvious regarding the increase of the activity in the series of cyclohexylamine (compound 6), cycloheptylamine (7) and cyclooctylamine (8) derivatives [6]. These differences could result from dissimilarities in the hydrolysis kinetics, since dichloroplatinum(II) complexes get their antitumor activities after hydrolysis into reactive species,

e.g. cisplatin hydrolyses to $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})\text{Cl}]^+$ and $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2]^{2+}$ [7]. The rate of this reaction depends on the strength of the bond between platinum and the leaving Cl^- ligand. This strength should be displayed in the electronic structure of the complex. Therefore, it is the subject of this investigation to study the influence of the coordinating ligands on the electronic structure by absorption, excitation, emission spectra and emission lifetime measurements.

Moreover, since the crystallographic unit cells of compounds 5, 7 and 8 are not known and since compound 6 is discussed controversially [8–10], we have redetermined the unit cells of the compounds 3, 4 and 6 and determined for the first time the ones of compounds 5, 7 and 8 in all cases from powder diffraction measurements.

Experimental

Preparation and analytical data (elemental analysis and ^1H NMR spectra) of the complexes are reported elsewhere [6].

Excitation spectra were recorded using a monochromatic light source which consists mainly of an XBO 75 W/2 short arc xenon lamp as radiation source and a monochromator (dispersion 4 nm/mm). Absorption spectra of the complexes dissolved in acetonitrile (Merck, uvasol) ($c \approx 5 \times 10^{-4}$ mol l^{-1}) and dimethyl-

*Present address: Department of Chemistry, University of California, Berkeley, CA 94720, USA.

**Authors to whom correspondence should be addressed.

TABLE 1. List of the studied compounds $\text{PtCl}_2(\text{RNH}_2)_2$

Compound	RNH_2	Complex
3	$\text{C}_3\text{H}_5\text{NH}_2$	<i>cis</i> -dichlorobis(cyclopropylamine)platinum(II)
4	$\text{C}_4\text{H}_7\text{NH}_2$	<i>cis</i> -dichlorobis(cyclobutylamine)platinum(II)
5	$\text{C}_5\text{H}_9\text{NH}_2$	<i>cis</i> -dichlorobis(cyclopentylamine)platinum(II)
6	$\text{C}_6\text{H}_{11}\text{NH}_2$	<i>cis</i> -dichlorobis(cyclohexylamine)platinum(II)
7	$\text{C}_7\text{H}_{13}\text{NH}_2$	<i>cis</i> -dichlorobis(cycloheptylamine)platinum(II)
8	$\text{C}_8\text{H}_{15}\text{NH}_2$	<i>cis</i> -dichlorobis(cyclooctylamine)platinum(II)
9	$\text{C}_7\text{H}_{13}\text{NH}_2$	<i>trans</i> -dichlorobis(cycloheptylamine)platinum(II)

formamide (DMF; Merck, uvasol) ($c \approx 10^{-2} \text{ mol l}^{-1}$) were recorded using a Uvikon 960 (Kontron) and a Shimadzu 210UV spectrophotometer, respectively. Emission spectra were recorded using an Ar^+ laser (Coherent Innova 90) as excitation source, a liquid helium bath cryostat (Oxford Company, GB), and a spectrometer described in ref. 11. The emission spectra were corrected for the spectral response of the monochromator and the photomultiplier (EMI 9659 QB S-20 extended, cooled to -30°C by a Joule–Thomson cooling system, Seefelder Meßtechnik, D-8031 Seefeld). Lifetime measurements were performed with the time resolved photocounting method (multiscaler from CMTE Fast Daten Systeme, D-8024 Oberhaching). Further details of the experimental technique are described elsewhere [11].

The powder diffraction patterns were recorded with a focusing monochromatic (Ge-monochromator, $\text{Cu K}\alpha_1$ radiation, $\lambda = 1.54056 \text{ \AA}$) transmission diffractometer STOE STADIP. The detector was a linear position sensitive detector covering a 2θ range of $\approx 4^\circ$. Flat specimens were measured in the $2\theta/\omega$ scan mode with a final resolution of $2\theta = 0.02^\circ$. Data handling was performed with the STOE software package including peak picking, search of the unit cell and subsequent refining of the unit cell constants [12].

Results

X-ray measurements

We have indexed powder diffraction patterns for compounds **3–8** (defined in Table 1). All diagrams except the one for compound **3** show one dominating peak and weak intensities combined with obviously strong overlap of the remaining reflections. Therefore, indexes of the reflections and evaluated unit cell parameters have to be inspected carefully. We could reproduce the known cell constants of compounds **3** and **4** [13, 14] with fairly good agreement. For the other compounds the best results were obtained with monoclinic unit cells, as has been found for compounds **3** and **4**. The refined lattice constants are summarized

in Table 2. The volumes of the unit cells (V), the atomic volumes of the non-hydrogen atoms (AV), and criteria of fit quality (quotient of numbers of observed reflections to possible reflections ($N_{\text{obs}}/N_{\text{poss}}$), figures of merit ($F(N_{\text{obs}})$) [15]) are listed in Table 3.

Spectroscopy

Excitation spectra of powder samples of compounds **4–8** were recorded in the range 250–500 nm ($\lambda_{\text{det}} = 580 \text{ nm}$, $T = 1.8 \text{ K}$). All compounds exhibit two broad bands lying near 27 000 and 32 000 cm^{-1} , respectively

TABLE 2. Lattice constants of *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes. The compounds are specified in Table 1

Compound	a (\AA) ^a	b (\AA)	c (\AA)	β ($^\circ$)	Reference
3	12.883(3)	5.400(1)	15.307(3)	104.69(1)	this work
3	12.770(5)	5.838(2)	15.113(6)	104.46(3)	13
4	5.975(2)	20.510(9)	11.491(5)	116.18(5)	this work
4	5.975(2)	20.459(8)	11.512(2)	116.18(2)	14
5	5.775(4)	23.15(1)	10.30(1)	95.75(9)	this work
6	24.49(3)	7.372(6)	10.99(1)	92.40(5)	this work
6	26.12(2)	6.660(6)	8.981(8)	90	8
7	25.68(2)	6.701(5)	13.51(1)	92.54(5)	this work
8	28.34(2)	6.934(5)	12.04(1)	104.35(4)	this work

^aNumbers in parentheses are e.s.d.s in the last significant digits.

TABLE 3. List of the unit cell volumes (V), atomic volumes (AV), and fit criteria of *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes. The compounds are specified in Table 1

Compound	V (\AA^3) ^a	AV ^b (\AA^3)	$N_{\text{obs}}/N_{\text{poss}}$	$F(N_{\text{obs}})$ ^c
3	1030.1(2)	23.4	27/137	31.8
4	1263.6(8)	24.3	26/188	10.6
5	1370(1)	22.8	19/85	10.3
6	1982(5)	29.1	25/148	13.0
7	2322(5)	30.6	22/170	11.7
8	2292(5)	27.3	23/160	14.0

^aNumbers in parentheses are e.s.d.s in the last significant digits. ^bAtomic volumes of the non-hydrogen atoms.

^c $F(N_{\text{obs}}) = (1/\sigma(2\theta)) \times (N_{\text{obs}}/N_{\text{poss}})$; N_{obs} : no. of observed reflections; N_{poss} : no. of possible reflections.

(Table 4). An excitation spectrum of compound **3** could not be recorded because of the low emission intensity with the XBO xenon lamp as excitation source.

The absorption spectra of the title compounds dissolved in dimethylformamide were recorded from 500 to 280 nm using concentrations of 10^{-2} mol l $^{-1}$ ($T \approx 300$ K). Moreover, for measurement of absorption spectra for $\lambda \leq 350$ nm the complexes were dissolved in acetonitrile in concentrations of 5×10^{-4} mol l $^{-1}$ ($T \approx 300$ K). The energy positions, halfwidths and ϵ values of the observed bands are listed in Table 4. To give an example, the absorption spectra of compound **7** dissolved in dimethylformamide and in acetonitrile, respectively, are shown in Fig. 1.

The emission spectra of compounds **3–8** in frozen dimethylformamide (DMF, $c \approx 10^{-3}$ mol l $^{-1}$) were recorded in the temperature range 1.8–80 K. A detection at higher temperatures was not possible because of the

low emission intensities. The energy positions and halfwidths of the emission spectra at $T = 1.8$ K are listed in Table 5. All compounds exhibit broad luminescence bands between $\approx 16\,500$ and $\approx 16\,800$ cm $^{-1}$ with halfwidths of about 2800 cm $^{-1}$. As an example, the emission spectrum of compound **7** dissolved in dimethylformamide ($T = 1.8$ K) is shown in Fig. 1. A temperature increase up to 80 K leads to a strong decrease of the emission intensities but no shifts of the energy positions are observed.

The luminescence spectra of powder samples of all the compounds could be detected in the temperature range 1.8–250 K. A detection at still higher temperatures was not possible, again because of the low intensities. Complexes **4–8** exhibit emission bands between 16 550 and 16 800 cm $^{-1}$ with halfwidths of about 2700 cm $^{-1}$ at $T = 1.8$ K (Table 5). A temperature increase causes decreasing intensities and again no shifts of the energy

TABLE 4. Bands^a in excitation^b and absorption^c spectra of *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes^d. The compounds are specified in Table 1

Compound	Excitation $\tilde{\nu}_{\max}$ (cm $^{-1}$)	Absorption		
		$\tilde{\nu}_{\max}$ (cm $^{-1}$)	ϵ (l mol $^{-1}$ cm $^{-1}$)	$\Delta\tilde{\nu}_{1/2}$ (cm $^{-1}$)
3		27000 ^e	35 ^e	3500 ^e
		27450	40	4500
		31150	85	3000
		35800	250	3500
		47100	7000	4000
4	27000	27350	40	4000
	32100	31700	120	3500
		35800	170	3500
		47100	7900	4000
5	27300	27500	40	4500
	32600	31700	80	3000
		36100	170	4000
		47200	5600	4000
6	27300	27300	40	4000
	32400	31700	80	3000
		36100	170	4000
		47300	6800	4500
7	27000	27600	35	4500
	32600	31600	80	4000
		36100	120	4000
		47200	6900	4000
8	27000	27500	50	4500
	31800	31600	100	4000
		36200	130	4000
		47200	7000	4000

^aEnergy positions, halfwidths, and ϵ values were determined by Gaussian fits; experimental errors: ± 100 cm $^{-1}$ for energy positions and halfwidths and $\pm 10\%$ for ϵ values. ^bPowder samples ($\lambda_{\text{det}} = 580$ nm; $T = 1.8$ K). ^cThe compounds were dissolved in dimethylformamide for the range 500–280 nm ($c \approx 10^{-2}$ mol l $^{-1}$; $T \approx 300$ K) and in acetonitrile for the range 350–200 nm ($c \approx 5 \times 10^{-4}$ mol l $^{-1}$; $T \approx 300$ K). ^dFor comparison: *cis*-Pt(NH $_3$) $_2$ Cl $_2$ (cisplatin) shows absorption (cm $^{-1}$) at 27000 ($\epsilon = 25$ l mol $^{-1}$ cm $^{-1}$), 32500 ($\epsilon = 170$ l mol $^{-1}$ cm $^{-1}$), 35500 ($\epsilon = 110$ l mol $^{-1}$ cm $^{-1}$), 45500 ($\epsilon = 2000$ l mol $^{-1}$ cm $^{-1}$) and 49500 ($\epsilon = 7500$ l mol $^{-1}$ cm $^{-1}$) [16]. ^eSingle crystal absorption spectrum (thickness of the crystal ≈ 15 μ m).

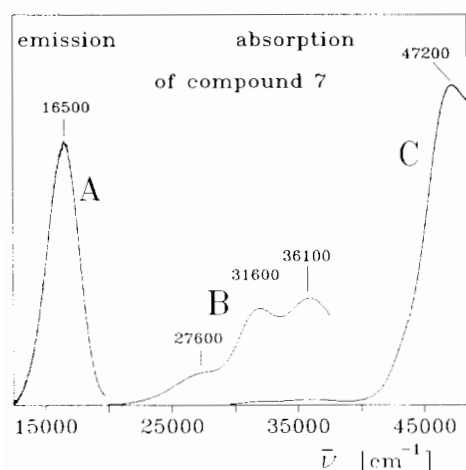


Fig. 1. Emission and absorption spectra of dissolved *cis*-dichlorobis(cycloheptylamine)platinum(II) (compound 7) as representative example. The dissolved compounds 3–6 and 8 exhibit largely the same spectra. A: emission spectrum dissolved in dimethylformamide ($c \approx 10^{-3}$ mol l $^{-1}$; $T = 1.8$ K). B: absorption spectrum dissolved in dimethylformamide ($c \approx 10^{-2}$ mol l $^{-1}$; $T \approx 300$ K). C: absorption spectrum dissolved in acetonitrile ($c \approx 5 \times 10^{-4}$ mol l $^{-1}$; $T \approx 300$ K).

positions as found for the dissolved complexes. The emission spectrum of a powder of compound 3 differs from those of the other compounds 4–8 and also from that of compound 3 dissolved in DMF. The maximum of the powder emission occurs at $\approx 15\,300$ cm $^{-1}$ with a halfwidth of about 4600 cm $^{-1}$ compared to $16\,700$ cm $^{-1}$ and a halfwidth of ≈ 2700 cm $^{-1}$ for the dissolved compound. The emission intensity of the powder sample of compound 3 decreases also with increasing temperature and no shift of the energy position is observed.

The emission lifetimes of powder samples were determined for all compounds in the temperature range 1.8–120 K. For compounds 4–8 emission lifetimes are monoexponential and lie between (22 ± 5) and (33 ± 5)

μ s at $T = 1.8$ K (Table 5). With increasing temperature the emission lifetimes of all the compounds become shorter (≈ 15 μ s (60 K), ≈ 10 μ s (120 K)). Compound 3 exhibits two significantly different lifetimes of (15 ± 5) and (62 ± 5) μ s at $T = 1.8$ K. But at higher temperature one observes only one component (≈ 8 μ s at 60 K, ≈ 3 μ s at 120 K).

We also recorded the luminescence of a powder sample of *trans*-dichlorobis(cycloheptylamine)-platinum(II) (compound 9). The spectrum shows a fine structure ($T = 1.8$ K), exhibiting a constant energy difference between local maxima of (310 ± 10) cm $^{-1}$ (progression) (Fig. 2). With increasing temperature the luminescence intensity decreases and the progression is smeared out. The emission lifetime of compound 9 is (50 ± 5) μ s at 1.8 K (Table 5).

We used the 364, 457, 488 and 514 nm lines, respectively, of an Ar $^{+}$ laser for excitation of the powder samples. The variation of the laser wavelength has no effect on the energies and halfwidths of the emission peaks.

Discussion

X-ray measurements

Despite the fact that indexing of the powder patterns was difficult, the given unit cell dimensions are satisfactory (the values of figure of merit are larger than ten, which indicates a sufficient quality of the fit [15]). The atomic volumes of the non-hydrogen atoms are somewhat larger for compounds 6, 7 and 8 compared with 3, 4 and 5. This behaviour could be due to steric hindrance between the cycloalkylamine ligands in *cis*-position. The unit cell dimensions determined for *cis*-dichlorobis(cyclohexylamine)platinum(II) (compound 6) differ significantly from those reported by Iball and

TABLE 5. Emission bands^a and emission lifetimes^a of dichlorobis(cycloalkylamine)platinum(II) compounds ($T = 1.8$ K) from powder samples and dissolved in DMF. The compounds are specified in Table 1

Compound	Powder samples			DMF ($c \approx 10^{-3}$ mol/l)	
	$\bar{\nu}_{\max}$ (cm $^{-1}$)	Halfwidth $\Delta\bar{\nu}_{1/2}$ (cm $^{-1}$)	Lifetime (μ s)	$\bar{\nu}_{\max}$ (cm $^{-1}$)	Halfwidth $\Delta\bar{\nu}_{1/2}$ (cm $^{-1}$)
3	15300	4600	15, 62	16700 ^b	2700
4	16750	2500	33	16800	2600
5	16800	2800	25	16750	2800
6	16550	2800	23	16550	2900
7	16550	2600	22	16500	2800
8	16800	2600	24	16700	2900
9	15900	2500	50		

^aExperimental errors: ± 100 cm $^{-1}$ for energy positions and halfwidths and ± 5 μ s for lifetimes. ^bFor comparison: *cis*-Pt(NH $_3$) $_2$ Cl $_2$ (cisplatin) dissolved in DMF ($T = 78$ K) shows luminescence at $\bar{\nu}_{\max} = 16950$ cm $^{-1}$ [16].

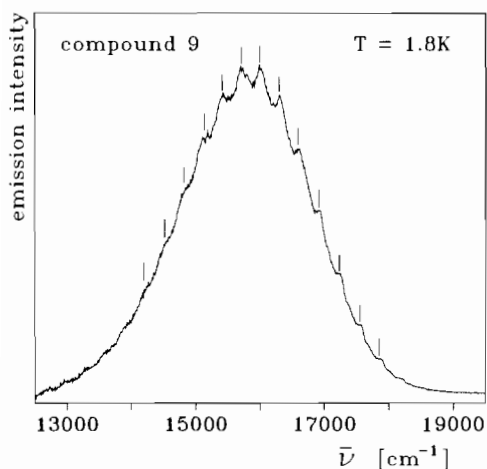


Fig. 2. Emission spectrum of a powder sample of *trans*-dichlorobis(cycloheptylamine)platinum(II) (compound 9) ($T=1.8$ K). The spectrum exhibits a progression of (310 ± 10) cm^{-1} .

Scrimgeour [8] (see Table 2). Independently, Zanotti *et al.* determined the structure of *trans*-dichlorobis(cyclohexylamine)platinum(II) [9]. The space group and unit cell dimensions of this *trans*-compound are exactly the same as those reported by Iball and Scrimgeour for the *cis*-compound. Further, Lock *et al.* [10] reported that the atom positions of the *cis*-form of dichlorobis(cyclohexylamine)platinum(II) (compound 6) can be converted into those of the *trans*-form by transferring (x, y, z) into $(x, -y, \frac{1}{2} + z)$ and renumbering the C atoms. Thus, they concluded that the structure reported by Iball and Scrimgeour [8] is probably an incorrect solution of the structure of the *trans*-compound. On the other hand, we found that compounds 7 and 8 are transformed into their corresponding *trans*-isomers during the process of recrystallization [6]. Lock and Zvagulis [14] reported the same behaviour for compound 4. Consequently, the structure determination by Iball and Scrimgeour [8] is regarded to be incorrect. Presumably, the '*cis*-compound 6' used by these authors had transformed during the process of recrystallization into the *trans*-isomer. Thus, it is more reasonable to assign *cis*-dichlorobis(cyclohexylamine)platinum(II) to a monoclinic structure.

Spectroscopy

The electronic spectra of a number of platinum(II) compounds with halides and primary amines as ligands are reported in the literature [16–20]. Absorption bands with $\bar{\nu} > 40\,000$ cm^{-1} and $\epsilon > 2000$ $\text{l mol}^{-1} \text{cm}^{-1}$ are assigned to $5d \rightarrow 6p$ transitions [16, 17, 21] and alternatively to $L(\pi) \rightarrow 5d$ transitions [19, 20]. Corresponding transitions are also found for *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes; they lie near

$47\,200$ cm^{-1} with ϵ values between 5600 and 7900 $\text{l mol}^{-1} \text{cm}^{-1}$ (Table 4).

Absorption bands with $\bar{\nu} < 40\,000$ cm^{-1} of the complexes $[\text{Pt}(\text{NH}_3)_n\text{Cl}_{4-n}]^{(n-2)+}$ with $n=0$ to 4 [16–18], $[\text{Pt}(\text{ethylenediamine})\text{X}_2]$ with $\text{X}=\text{Cl}, \text{Br}$ [19, 20], and $[\text{Pt}(\text{piperidine})\text{Cl}_2]$ [18] are assigned to d–d transitions. Several authors try to give detailed group-theoretical classifications and distinguish in part between absorptions with $\epsilon < 50$ $\text{l mol}^{-1} \text{cm}^{-1}$ and absorptions with ϵ values larger than 60 $\text{l mol}^{-1} \text{cm}^{-1}$, by assigning the first ones to spin-forbidden d–d transitions, and the latter ones to spin-allowed d–d transitions. However, for heavy metal atoms spin–orbit coupling causes a strong mixture of singlet and triplet states. Therefore a clear distinction between singlets and triplets appears to be problematic, especially given the small differences of the observed ϵ values. The absorption spectrum of each *cis*-dichlorobis(cycloalkylamine)platinum(II) compound exhibits bands in this energy range at about $27\,500$, $31\,500$ and $36\,000$ cm^{-1} (Table 4 and Fig. 1). The ϵ values lie between 30 and 250 $\text{l mol}^{-1} \text{cm}^{-1}$. Such values are typical for d–d transitions [16–20]. Therefore, we assign the absorptions with $\bar{\nu} < 40\,000$ cm^{-1} of compounds 3–8 to d–d transitions.

We also investigated the luminescence of compounds 3–8 in frozen DMF. The energy positions of the emission peaks are very similar to each other and to the one reported for *cis*- $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ [16] (Table 5). Thus, replacement of the amine ligands by cycloalkylamines has no significant effect on the LUMO–HOMO transitions of these platinum(II) complexes.

The luminescence of powder samples of compounds 4–8 lies close to that observed in DMF (Table 5). In contrast, the emission of compound 3 (powder) is appreciably broadened from a halfwidth of 2700 cm^{-1} to about 4600 cm^{-1} and the peak maximum appears to be red-shifted from $\approx 16\,700$ to $\approx 15\,300$ cm^{-1} . However, compound 3 shows a similar behaviour in absorption and emission in frozen DMF as compounds 4–8. Thus, the different properties of the powder samples of compound 3 indicate the existence of solid state effects and/or the influence of impurities.

The emission lifetimes of compounds 3–8 are longer than 10 μs as is typical of spin-forbidden transitions. The symmetry of the ligand field around Pt(II) in *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes is approximately C_{2v} [10, 13, 14]. According to refs. 16–20 the HOMO and the LUMO result mainly from $d_{y^2-z^2}$ (a_1) and d_{yz} (b_2) orbitals, respectively (x axis contains the Pt atom and is perpendicular to the molecular plane, z axis bisects the angle N–Pt–N). From this it is deduced that the emitting many-electron state of compounds 3–8 is a sublevel of 3B_2 , but we do not exclude admixtures of states from other configurations (e.g. ref. 22).

For all *cis*-dichlorobis(cycloalkylamine)platinum(II) complexes the peak position of the emission occurs by $\approx 11\,000\text{ cm}^{-1}$ to the red compared to the absorption (excitation) peak with lowest energy (Fig. 1). This value seems to be too large for a Stokes shift. For example, tetrachloro-, tetrabromo- and tetrathiocyanato complexes of platinum(II) exhibit a Stokes shift of $\approx 5000\text{ cm}^{-1}$ [23]. This indicates, that a further state (the emitting one) – leading to a strongly forbidden transition – should be present.

Moreover, using the relation between the radiative lifetime τ_{rad} and the observed absorption at lowest energy (approximation for symmetrical bands) [24]

$$\tau_{\text{rad}}(\text{s}) = \frac{3.5 \times 10^8}{\bar{\nu}_m^2 \epsilon_m \Delta \bar{\nu}_{1/2}}$$

where $\bar{\nu}_m$ is the mean energy (cm^{-1}) of the absorption band, ϵ_m is the maximum extinction coefficient ($\text{l mol}^{-1}\text{ cm}^{-1}$) and $\Delta \bar{\nu}_{1/2}$ is the halfwidth (cm^{-1}) of the band, we can give an estimate for the radiative lifetime, which represents the upper limit for the emission lifetime. Using the values of compounds 3–8 (e.g. compound 4: $\bar{\nu}_m = 27\,350\text{ cm}^{-1}$, $\epsilon_m = 40\text{ l mol}^{-1}\text{ cm}^{-1}$, $\Delta \bar{\nu}_{1/2} = 4000\text{ cm}^{-1}$; see Table 4) one obtains $\tau_{\text{rad}} \approx 3\text{ }\mu\text{s}$. We roughly checked that the quantum yield Φ is smaller than 0.1. Thus, the corresponding lifetime has to be smaller than $0.3\text{ }\mu\text{s}$. The experimental values, however, are nearly two orders of magnitude larger. Consequently, we conclude that the detected absorption at $\approx 27\,500\text{ cm}^{-1}$ does not correspond to the emitting transition.

Nevertheless, a Stokes shift of $\approx 5000\text{ cm}^{-1}$ [23] indicates a strong distortion of the excited state. For several other compounds it is possible to describe this distortion more quantitatively by a Franck–Condon analysis [25, 26]. However, the emission bands of 3–8 exhibit no fine structure. On the other hand, the related *trans*-dichlorobis(cycloheptylamine)platinum(II) (9) exhibits a clearly observable progression of ≈ 15 modes in the emission band (Fig. 2). The progression occurs with a value of $\approx 310\text{ cm}^{-1}$ which is at the lower end of the region typical of Pt–Cl stretching vibrations [13, 27–29]. From the spectrum we can estimate the value of the Huang Rhys factor [30] to be about 10, which indicates a very strong distortion of the molecular geometry of the excited state relative to the ground state. *Cis*- and *trans*-isomers of platinum(II) compounds exhibit similar values for Stokes shifts and halfwidths [16–18]. Therefore, we assume that the *cis*-isomers are similar to compound 9 in this respect.

Conclusions

The optical properties of the discussed *cis*-PtCl₂(RNH₂)₂ are very similar to each other. The

properties of the highest occupied and lowest unoccupied orbitals, which are mainly of platinum d character, are only slightly influenced by a variation of the amine ligands. The strongly different behavior of compounds 3–8 in tests against the human MDA-MB-231 breast cancer cell line [6] are not reflected in these spectroscopic properties.

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References

- 1 B. Rosenberg, L. VanCamp and T. Krigas, *Nature (London)*, 205 (1965) 698.
- 2 B. Rosenberg, L. VanCamp, J. E. Trosko and V. H. Mansour, *Nature (London)*, 222 (1969) 385.
- 3 C. A. Lepre and S. J. Lippard, in F. Eckstein and D. M. J. Lilley (eds.), *Nucleic Acids and Molecular Biology*, Vol. 4, Springer, Berlin, 1990, p. 11.
- 4 S. E. Sherman and S. J. Lippard, *Chem. Rev.*, 87 (1987) 1153.
- 5 J. Reedijk, A. M. J. Fichtinger-Schepman, A. T. van Oosterom and P. van de Putte, *Struct. Bonding (Berlin)*, 67 (1987) 53.
- 6 J. Kritzenberger, G. Bernhardt, R. Gust, P. Pistor, H. Schönnenberger and H. Yersin, *Monatsh. Chem.*, in press.
- 7 J. Reedijk, *Pure Appl. Chem.*, 59 (1987) 181.
- 8 J. Iball and S. N. Scrimgeour, *Acta Crystallogr., Sect. B*, 33 (1977) 1194.
- 9 G. Zanotti, A. Del Pra, G. Bombieri and A. M. Tamburro, *Acta Crystallogr., Sect. B*, 34 (1978) 2138.
- 10 C. J. L. Lock, R. A. Speranzini and M. Zvagulis, *Acta Crystallogr., Sect. B*, 36 (1980) 1789.
- 11 (a) H. Yersin and G. Gliemann, *Messtechnik*, 80 (1972) 99; (b) M. Stock and H. Yersin, *Chem. Phys. Lett.*, 40 (1976) 423.
- 12 *STOE Powder Software Manual*, STOE & CIE, Darmstadt, 1990.
- 13 H. E. Howard-Lock, C. J. L. Lock, G. Turner and M. Zvagulis, *Can. J. Chem.*, 59 (1981) 2737.
- 14 C. J. L. Lock and M. Zvagulis, *Inorg. Chem.*, 20 (1981) 1817.
- 15 G. S. Smith and R. L. Snyder, *J. Appl. Crystallogr.*, 12 (1979) 60.
- 16 H. H. Patterson, J. C. Tewksbury, M. Martin, M.-B. Krogh-Jespersen, J. A. LoMenzo, H. O. Hooper and A. K. Viswanath, *Inorg. Chem.*, 20 (1981) 2297.
- 17 J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, (1958) 486.
- 18 M. Textor and W. Ludwig, *Helv. Chim. Acta*, 55 (1972) 184.
- 19 D. S. Martin, Jr., L. D. Hunter, R. Kroening and R. F. Coley, *J. Am. Chem. Soc.*, 93 (1971) 5433.
- 20 R. F. Kroening, L. D. Hunter, R. M. Rush, J. C. Clardy and D. S. Martin, Jr., *J. Phys. Chem.*, 77 (1973) 3077.
- 21 B. D. El-Issa, M. A. Makhyouan and B. A. Salsa, *Int. J. Quantum Chem.*, 31 (1987) 295.
- 22 L. Viaene, A. Ceulemans and L. G. Vanquickenborne, *Inorg. Chem.*, 24 (1985) 1713.

- 23 W. Tuszynski, G. Gliemann, *Z. Naturforsch., Teil A*, 34 (1979) 211.
- 24 N. J. Turro, *Molecular Photochemistry*, W. A. Benjamin, Amsterdam, 1967, p. 48.
- 25 G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. 1, Van Nostrand, New York, 1950, Ch. IV.
- 26 H. Yersin, H. Otto, J. I. Zink and G. Gliemann, *J. Am. Chem. Soc.*, 102 (1980) 951.
- 27 T. Boschi, G. Deganello and G. Carturan, *J. Inorg. Nucl. Chem.*, 31 (1969) 2423.
- 28 D. M. Adams, J. Chatt, J. Gerratt and A. D. Westland, *J. Chem. Soc.*, (1964) 734.
- 29 O. M. Adamov, A. I. Stetsenko, I. B. Pushko and V. G. Pogareva, *Koord. Khim.*, 16 (1990) 455 (in English).
- 30 B. Henderson and G. F. Imbusch, *Optical Spectroscopy of Inorganic Solids*, Clarendon, Oxford, 1989, p. 202.