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Crystal Structures and Spectroscopic Properties of *trans-N,P*-[Pt(ppy)($Pmor_3$)Cl] and *trans-N,P*-[Pt(tpy)($Pmor_3$)Cl]·CH_3CN [ppy = *N,C′*-chelated 2-phenylpyridinate, tpy = *N,C′*-chelated 2-(2′-thienyl)pyridinate, $Pmor_3$ = tris(morpholino)phosphine]

Konstantin P. Balashev,[a] Thoralf Engebretsen,[b,*] Per-Inge Kvam,[b] Knut Maartmann-Moe,[b] Michael V. Puzyk[a] and Jon Songstad[b]

[a]Department of Chemistry, Russia State Pedagogical University, 191186 St. Petersburg, Russia and [b] Department of Chemistry, University of Bergen, N-5007 Bergen, Norway

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The crystal structures of [Pt(ppy)($Pmor_3$)Cl], **I**, and [Pt(tpy)-($Pmor_3$)Cl]·CH_3CN, **II**, have been determined at 93 K. **I** crystallizes in the $P2_1/a$ space group with the following unit-cell dimensions: $a = 17.192(5)$, $b = 15.593(2)$ and $c = 18.178(4)$ Å, $\beta = 91.27(2)°$, $V = 4879(3)$ Å^3, $Z = 8$. $R = 0.031$, ($R_w = 0.028$) for 8573 unique reflections. There are two molecules, **Ia** and **Ib**, in the asymmetric unit. Compound **II** crystallizes in the same space group, $a = 12.415(4)$, $b = 12.731(4)$ and $c = 16.702(6)$ Å, $\beta = 105.42(2)°$, $V = 2543(2)$ Å^3, $Z = 4$. $R = 0.026$ ($R_w = 0.033$) for 6396 unique reflections. The phosphorus ligand is located *trans* to the nitrogen atom of the cyclometalated ligand with a Pt–N bond length of 2.106(5) Å in **Ia** 2.111(5) in **Ib** and 2.134(3) Å in **II**. Long-wave absorption bands in the absorption spectra of **I** and **II** have been assigned to metal-to-ligand charge transfer (MLCT) transitions, while higher energy bands have been assigned to ligand-centered (LC) transitions. Compound **II** shows strong emission in solution at room temperature. The presence of the large phosphorus ligand leads to long Pt–Pt distances, the shortest being 5.988(5) Å in **I** and 7.777(4) Å in **II**, preserving monomeric type of electronic structure of the complexes both in solution and in the solid state.

The design and study of unsaturated four-coordinated d^8 metal complexes with long-lived excited states have been in focus in recent years. A number of Ir^I, Rh^I, Pd^{II} and Pt^{II} complexes with ligands like diphosphines,[1,2] α,α′-diimines[3] and dithiolates[4] have been prepared and examined in search for species being luminiscent, preferably at room temperature. A related class of compounds with structurally similar ligands with one aromatic carbon atom linked to the central atom has been shown to be promising.[5–8] Pt^{II} complexes of this type, [Pt⟨N–C⟩AB]^z, where ⟨N–C⟩ represents deprotonated 2-phenylpyridine, ppy, 2-(2′-thienyl)pyridine, tpy, or related ligands, and where A and B are various monodentate and bidentate ligands, appear particularly interesting due their high ligand field strength and the character of their lowest excited state.[7,9,10] An interesting feature of these square-planar luminophores is their tendency to form ground-state oligomers and excimers.[11–13] An electronic interaction between monomers in the solution and particularly in the solid state may have significant effects upon absorption and emission properties of this kind of species and may lead to some cooperative excited structures.

Salts of anions like [Pt⟨N–C⟩Cl_2]$^-$ are not luminiscent at room temperature but are readily transformed into mixed-ligand Pt^{II} complexes, [Pt⟨N–C⟩AB]^z.[8,11,12] As part of a study of the influence of donor and acceptor properties of A and B ligands upon the photophysical behaviour of this class of complexes,[11] we have turned to compounds with tervalent phosphorus ligands, *trans-N,P*-[Pt⟨N–C⟩(PR_3)Cl], compounds which are readily formed at room temperature, [eqn. (1)]:[8,14]

$$[Pt\langle N\text{–}C\rangle Cl_2]^- + PR_3 \rightarrow \textit{trans-N,P}\text{-}[Pt\langle N\text{–}C\rangle(PR_3)Cl] \quad (1)$$

* To whom correspondence should be addressed.

These compounds are stable in the solid state and when dissolved in the usual organic solvents. When tervalent phosphorus is used as the incoming ligand the donor and acceptor properties[15] and also the steric demands[16] can be varied significantly. An additional interesting feature of these reactions is the unusual *trans* effect of the cyclometalated ligands. One would anticipate the chloride *trans* to the carbon atom in $[Pt\langle N\text{–}C\rangle Cl_2]^-$ to be the more labile one. However, from all substitution reactions which so far have been examined, with one notable exception,[17] only compounds with the entering ligand located *trans* to the nitrogen atom have been isolated.[8,10,12,14,18] In the present study we want to report on the crystal structures and the spectroscopic properties of the products, **I** and **II**, from the reaction between $Bu_4N[Pt\langle N\text{–}C\rangle Cl_2]$ and tris(morpholino)phosphine, $Pmor_3$:

$\langle N\text{–}C\rangle$ = *N,C'*-chelated 2-phenylpyridinate, ppy **(I)**

$\langle N\text{–}C\rangle$ = *N,C'*-chelated 2-(2'-thienyl)pyridinate, tpy **(II)**

Tris(morpholino)phosphine was chosen as the phosphorus nucleophile owing to its simple purification,[19] its high nucleophilicity,[20] its known crystal structure,[21] its lack of aromatic hydrogen atoms allowing a detailed NMR study to be performed[8] and by the quality of the crystals obtained. Based upon the large Pt–P coupling contstants,[22] 5336 Hz in **I** and 5540 Hz in **II**, it was concluded that the tervalent phosphorus compound was located *trans* to the nitrogen atom.[8] The crystal structures of $Bu_4N[Pt(ppy)Cl_2]$ and $Et_4N[Pt(tpy)Cl_2]$ have recently been published.[23]

Experimental

The preparation of [Pt(ppy)(Pmor$_3$)Cl], **I**, and [Pt(tpy)(Pmor$_3$)Cl]·CH_3CN, **II**, has been described.[8] The yellow crystals of **I** and the orange crystals of **II** were grown from solutions in pure acetonitrile by slow cooling to −20 °C. Measurements of cell dimensions and intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å). The temperature at the crystal site during data collection was 93 K. Cell parameters were determined using a least-squares fit for 25 reflections.

The intensities were corrected for Lorentz and polarization effects, and variation in three standard reflections were used for scaling the intensity data. A semi-empirical psi-scan procedure was used to correct for absorption with transmissions factors varying from 99 to 73% in **I** and from 99 to 66% in **II**.[24] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques. Anisotropic temperature factors were applied to all non-hydrogen atoms except the solvent molecule in **II** and the aromatic carbon atoms in **I**. Since C11 in **I** was not found to refine with anisotropic thermal parameters all aromatic carbon atoms in this compound were treated isotropically. The origin for this difficulty may be the presence of a solvent molecule of low occupancy located close to C11. The hydrogen atoms were placed geometrically at a fixed C–H distance of 0.95 Å and were refined isotropically. All computer programs used belong to the Enraf-Nonius Molen package.[25] Atomic scattering factors were taken from Ref. 26. Structure-factor tables and thermal parameters are available from the authors. Fractional coordinates with estimated standard deviations together with isotropic equivalent thermal parameters, B_{eq}, are listed in Table 1.

Compound **I** was found to contain two molecules in the asymmetric unit. These two molecules are termed **Ia** and **Ib**. Crystal and experimental data together with final figures of merit for **I** and **II** are listed in Table 2.

Electronic absorption spectra were recorded on a Varian Cary1 UV–visible spectrophotometer. The instrumentation used to obtain emission spectra and lifetime data (estimated errors <10%) has been described.[11] Emission lifetimes were measured with a pulse nitrogen laser, LG1–21, as light source with $\lambda_{exc} = 337$ nm and a pulse half-width of 10 ns.[11] Emission quantum yields were estimated by the optical dilution method[27] using $[Ru(bipy)_3]^{2+}$ [27] and fluorescein[28] as standards and were corrected for differences in the refractive index of the solvents. The total error was estimated to be less than 30%.

Results and discussion

Description of the structures. Figure 1 shows drawings of **Ia**, **Ib** and **II** together with numbering of the atoms. For the sake of brevity the hydrogen atoms are omitted. Since the Pt atom and the four surrounding atoms do not form perfect planes, the molecules are presented with the Pt atom and the chelating N and C atoms in the plane of the paper. In **Ia** and **Ib** the Cl atom is 0.256(2) and 0.417(2) Å above, while the P atom is 0.206(2) and 0.239(2) Å below. In compound **II** the Cl and the P atoms are closer to the corresponding plane; the Cl atom being 0.043(1) Å below and the P atom 0.037(1) Å above. It is apparent from this study that the phosphorus ligand is located *trans* to the nitrogen atom of the *N,C*-ligands as was indeed concluded from the NMR experiments.[8] Owing to the size of the phosphorus ligand, the crystal packing leaves some large cavities which are occupied by a solvent molecule in **II**.

In all three molecules one of the morpholine nitrogen atoms is fairly close to the plane as defined by the Pt, N and C atoms, N4 being 0.595(5) Å below the plane in **Ia**, N7 0.480(5) Å below in **Ib** and N3 0.120(4) Å above in **II**. By this nearly '*trans*' arrangement of the chelating carbon atom and the one nitrogen atom; the C–Pt–P–N torsion angles being −166.8(3)° in **Ia**, +173.3(3)° in **Ib** and −177.3(4)° in **II**, the two remaining morpholine groups are scissoring the phenyl and the thienyl part of the *N,C*-chelated ligands to minimize steric interactions.

Table 1. Fractional coordinates and their estimated standard deviations of non-hydrogen atoms and equivalent isotropic temperature factors, B_{eq}, in Å^2.[a]

Atom	x	y	z	B_{eq}
Compound **I**				
Pt1	0.10863(2)	0.10751(2)	0.41241(1)	0.670(4)
Pt2	0.37321(2)	0.07458(2)	0.89494(1)	0.790(4)
Cl1	0.0905(1)	0.2278(1)	0.49148(9)	1.16(3)
Cl2	0.3699(1)	0.2062(1)	0.96168(9)	1.29(3)
P1	0.1859(1)	0.0443(1)	0.49651(9)	0.75(3)
P2	0.3144(1)	0.0022(1)	0.98299(9)	0.86(3)
O1	0.1405(3)	−0.2408(3)	0.5097(3)	1.4(1)
O2	0.4260(3)	−0.0032(3)	0.4292(2)	1.5(1)
O3	0.1711(3)	0.1236(3)	0.7350(2)	1.4(1)
O4	0.4165(3)	−0.2593(3)	1.0304(3)	2.1(1)
O5	0.3173(3)	0.1242(3)	1.2084(3)	1.8(1)
O6	0.0578(3)	−0.0301(3)	0.9337(2)	1.2(1)
N1	0.0278(3)	0.1583(3)	0.3353(3)	1.0(1)
N2	0.1633(3)	−0.0593(3)	0.5050(3)	0.9(1)
N3	0.2800(3)	0.0568(3)	0.4800(3)	0.8(1)
N4	0.1844(3)	0.0754(4)	0.5846(3)	0.8(1)
N5	0.4398(3)	0.1326(3)	0.8124(3)	1.0(1)
N6	0.3588(3)	−0.0904(3)	1.0048(3)	1.2(1)
N7	0.3094(3)	0.0452(4)	1.0672(3)	1.0(1)
N8	0.2211(3)	−0.0163(3)	0.9611(3)	0.9(1)
C1	−0.0202(4)	0.2245(4)	0.3461(4)	1.3(1)*
C2	−0.0730(4)	0.2517(4)	0.2938(4)	1.2(1)*
C3	−0.0771(4)	0.2088(5)	0.2275(4)	1.5(1)*
C4	−0.0289(4)	0.1416(5)	0.2154(4)	1.5(1)*
C5	0.0230(4)	0.1144(4)	0.2703(3)	1.0(1)*
C6	0.0746(4)	0.0402(4)	0.2668(4)	1.0(1)*
C7	0.0774(4)	−0.0136(4)	0.2060(4)	1.2(1)*
C8	0.1250(4)	−0.0844(4)	0.2042(3)	1.0(1)*
C9	0.1721(4)	−0.1015(5)	0.2654(4)	1.4(1)*
C10	0.1703(4)	−0.0488(4)	0.3259(4)	1.2(1)*
C11	0.1212(4)	0.0223(4)	0.3312(4)	1.0(1)*
C12	0.2005(4)	−0.1141(5)	0.5622(4)	1.3(1)
C13	0.2130(4)	−0.2021(5)	0.5323(4)	1.9(2)
C14	0.1035(4)	−0.1889(5)	0.4540(4)	1.5(1)
C15	0.0896(4)	−0.0984(4)	0.4805(4)	1.2(1)
C16	0.3456(4)	0.0368(5)	0.5302(4)	1.1(1)
C17	0.3966(4)	−0.0318(5)	0.4981(4)	1.4(1)
C18	0.3622(4)	0.0139(5)	0.3787(4)	1.5(1)
C19	0.3098(4)	0.0812(5)	0.4082(4)	1.4(1)
C20	0.2239(4)	0.1520(4)	0.6141(4)	1.0(1)
C21	0.2414(4)	0.1376(4)	0.6949(4)	1.2(1)
C22	0.1325(4)	0.0494(5)	0.7062(4)	1.6(2)
C23	0.1122(4)	0.0598(4)	0.6252(4)	1.0(1)
C24	0.4737(4)	0.2094(5)	0.8171(4)	1.4(1)*
C25	0.5186(4)	0.2409(5)	0.7608(4)	2.0(1)*
C26	0.5267(4)	0.1932(5)	0.6988(4)	1.8(1)*
C27	0.4924(4)	0.1140(5)	0.6932(4)	1.8(1)*
C28	0.4498(4)	0.0825(4)	0.7516(4)	1.3(1)*
C29	0.4111(4)	−0.0006(4)	0.7551(4)	1.1(1)*
C30	0.4127(4)	−0.0597(5)	0.6968(4)	1.6(1)*
C31	0.3708(4)	−0.1348(5)	0.6990(4)	1.7(1)*
C32	0.3263(4)	−0.1526(5)	0.7600(4)	1.8(1)*
C33	0.3269(4)	−0.0957(4)	0.8200(4)	1.4(1)*
C34	0.3680(4)	−0.0195(4)	0.8198(4)	1.0(1)*
C35	0.4312(4)	−0.1194(4)	0.9730(4)	1.3(1)
C36	0.4289(4)	−0.2155(5)	0.9618(4)	1.9(2)
C37	0.3452(4)	−0.2320(5)	1.0638(4)	2.2(2)
C38	0.3474(4)	−0.1353(5)	1.0755(4)	1.5(1)
C39	0.3854(4)	0.0647(4)	1.1043(4)	1.3(1)
C40	0.3752(4)	0.0635(5)	1.1862(4)	1.6(1)
C41	0.2445(4)	0.1049(5)	1.1724(4)	1.8(2)
C42	0.2509(4)	0.1077(5)	1.0894(4)	1.2(1)
C43	0.1785(4)	−0.0920(5)	0.9838(4)	1.6(2)
C44	0.0928(4)	−0.0696(5)	0.9964(4)	1.5(1)
C45	0.1003(4)	0.0462(5)	0.9156(4)	1.9(2)
C46	0.1841(4)	0.0263(5)	0.8990(4)	1.7(2)
Compound **II**				
Pt	0.07668(1)	0.01556(1)	0.28924(1)	0.527(2)
Cl	0.20421(8)	0.04876(8)	0.42016(5)	1.03(2)
S	−0.03344(8)	−0.12983(8)	0.03765(6)	1.14(2)
P	−0.06051(8)	0.11038(8)	0.31510(6)	0.64(2)
O1	−0.3521(2)	−0.0979(2)	0.3236(2)	1.22(5)
O2	−0.0031(3)	0.3008(2)	0.5507(2)	1.41(6)
O3	−0.1742(3)	0.3589(2)	0.1155(2)	1.39(6)
N1	0.1975(3)	−0.0769(3)	0.2510(2)	0.76(6)
N2	−0.1686(3)	0.0333(3)	0.3184(2)	0.81(6)
N3	−0.0450(3)	0.1796(3)	0.4030(2)	0.79(6)
N4	−0.0982(3)	0.2069(3)	0.2445(2)	0.89(6)
C1	0.3052(3)	−0.0931(3)	0.2933(2)	0.88(7)
C2	0.3766(3)	−0.1538(3)	0.2618(3)	1.22(8)
C3	0.3365(3)	−0.2017(3)	0.1849(2)	1.20(7)
C4	0.2265(4)	−0.1845(3)	0.1401(2)	1.32(8)
C5	0.1581(3)	−0.1212(3)	0.1742(2)	0.91(7)
C6	0.0433(3)	−0.0925(3)	0.1347(2)	0.94(7)
C7	−0.1450(3)	−0.0576(4)	0.0488(2)	1.20(7)
C8	−0.1230(3)	−0.0072(3)	0.1243(2)	1.03(7)
C9	−0.0140(3)	−0.0279(3)	0.1751(2)	0.71(7)
C10	−0.2806(3)	0.0772(3)	0.3085(3)	1.47(8)
C11	−0.3501(3)	0.0076(3)	0.3499(3)	1.46(8)
C12	−0.2404(3)	−0.1369(3)	0.3468(3)	1.19(8)
C13	−0.1697(3)	−0.0790(3)	0.3004(2)	1.02(7)
C14	−0.1681(3)	0.2974(3)	0.2534(2)	1.10(7)
C15	−0.2409(3)	0.3295(3)	0.1697(3)	1.22(8)
C16	−0.1080(3)	0.2708(3)	0.1043(2)	1.30(8)
C17	−0.0320(3)	0.2344(3)	0.1863(2)	0.96(7)
C18	−0.0549(3)	0.1332(3)	0.4811(2)	0.95(7)
C19	−0.0853(3)	0.2197(4)	0.5339(2)	1.25(8)
C20	0.0057(4)	0.3470(3)	0.4749(3)	1.21(8)
C21	0.0386(3)	0.2648(3)	0.4198(2)	0.91(7)
N5	0.3741(8)	−0.1006(7)	−0.0264(5)	5.9(2)*
C22	0.4437(8)	−0.0887(8)	0.0467(6)	4.5(2)*
C23	0.5255(6)	−0.0655(6)	0.1246(5)	3.2(1)*

[a] B factors marked * have been treated isotropically.
$B = \exp[-0.25(B_{11}h^2a^2 + B_{22}k^2b^2 + B_{33}l^2c^2 + B_{12}hkab^*\cos\gamma + 2B_{13}hlac^*\cos\beta + 2B_{23}klbc^*\cos\alpha]$.

It is notable that it is the morpholine group with its nitrogen atom of highest *p*-character, i.e. the group with largest steric demands, which is occupying the position '*cis*' to the chlorine atom in the three molecules. (The hybridization of the nitrogen atoms in the phosphorus ligand will be discussed below.)

Table 3 gives the most important bond lengths and bond angles in **Ia** and **II**. The structures of **Ia** and **Ib** differ only significantly with regard to the Cl–Pt–P bond angles, 90.04(6)° in **Ia** and 93.11(6)° in **Ib**, and the C–Pt–P bond angles, 98.0(2)° and 96.0(2)°. A further increase in the Cl–Pt–P bond angle is observed in **II**, in which this bond angle is 94.72(4)° while the C–Pt–P bond angle is reduced to 93.9(1)°. The decrease in the C–Pt–P bond angle and the increase in the Cl–Pt–P bond angle seem to be related to the steric interactions between the two morpholino groups and the phenyl and the thienyl parts of the aromatic ligands. Since the C–Pt–P–N torsion angle in **II** is close to the ideal one of 180° and the thienyl group in **II** is smaller than the phenyl group in **Ia** and **Ib** one may conclude that the

Table 2. Crystal and experimental data for **I** and **II**.

Compound	I	II
Formula	[Pt(ppy)(Pmor$_3$)Cl]	[Pt(tpy)(Pmor$_3$)Cl]·CH_3CN
M_w	677.1	724.2
M.p./°C	261 (dec)	243 (dec)
Radiation/scan mode	Mo-K_α/ω-scan	Mo-K_α/ω-scan
θ-range/°	$0<\theta<25$	$0<\theta<28$
Scan width ($x+0.34$ tan θ)/°	1.100	1.200
a/Å	17.192(5)	12.415(4)
b/Å	15.593(2)	12.731(1)
c/Å	18.178(4)	16.702(6)
β/°	91.27(2)	105.42(2)
V/Å^3	4879(3)	2543(2)
Space group	$P2_1/a$ (No.14)	$P2_1/a$ (No.14)
Z	8	4
d_{calc}/g cm^{-3}	1.964	1.883
Absorption coefficient/cm^{-1}	60.35	58.56
No. of unique reflections	8573	6396
No. of $I>3.0\sigma(I)$	6004	5178
$R=\Sigma\|F_o-F_c\|/\Sigma F_o$	0.031	0.026
$R_w=(\Sigma w_o F_o\|-\|F_c\|^2/\Sigma w\|F_2\|^2)^{0.5}$	0.028	0.033
$S=[\Sigma w(\Delta F)^2/(N-n)]^{0.5}$	1.216	1.626
k in weight scheme[a]	0.02	0.02

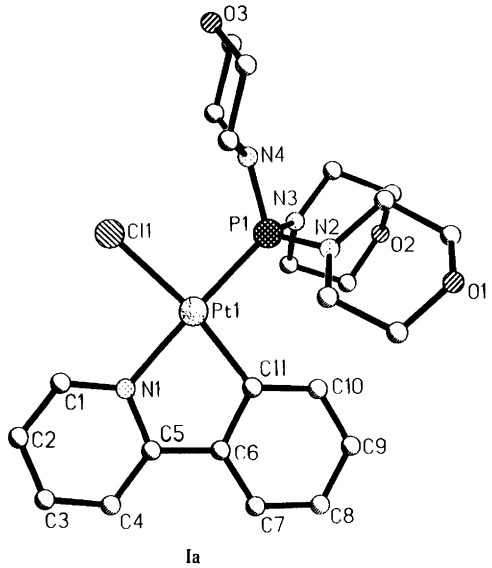
[a]Function minimized $\Sigma[w(|F_o|-|F_c|)^2]$, $w=4F_o^2/[\sigma_c^2+(kF_o^2)^2]$, where σ_c is the standard deviation in F^2 based on counting statistics alone.

structural parameters of **II** are the most representative ones for this class of compounds. It is notable that the N–Pt–C bite angle, ca. 80–81°, is fairly independent of the form of the molecules and the substituents and is close to what has been observed in several structural studies of cyclometalated compounds derived from 2-phenylpyridine and 2-(2′-thienyl)pyridine.[8,12,23]

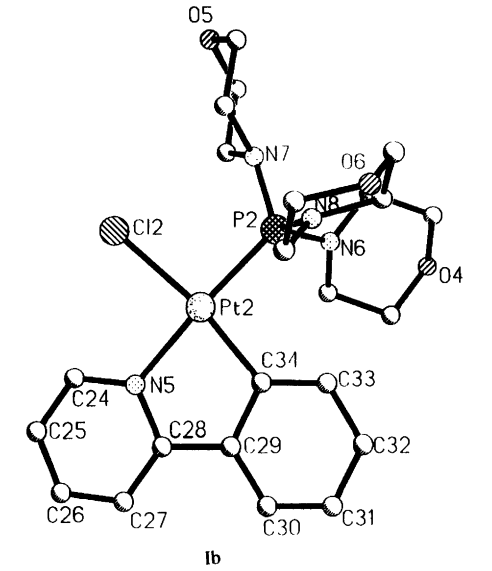
Apart from the minor differences mentioned above the molecules differ slightly with regard to the position of the Pt atoms relative to the planes defined by the phenyl (thienyl) rings and the pyridine rings. In **Ia** the Pt atom is exactly in the plane of the phenyl ring, while in **Ib** this atom is close to the plane of the pyridine ring. In **II** the Pt atom is located in the plane of both rings within experimental error. The *N,C′*-chelated ligands are not perfectly planar but the angle between the two ring planes is only 3.8(2.7)° in **Ia**, 3.3(3.0)° in **Ib** and 3.9(1.5)° in **II**. The magnitude of these angles and their experimental error are close to those observed in the corresponding dichloroanions, [Pt⟨N–C⟩Cl_2]$^-$.[23]

Intra- and intermolecular non-bonding distances. The molecules do not form layers or stacks as observed for *cis-C,C*-[Pt(tpy)(CO)Cl],[18] *cis-C,C*-[Pt(ptpy)(CO)Cl][12] (ptpy=cyclometalated 2-(4-Me-phenyl)pyridine) and [Pt(2,2′-bpy)Cl_2],[29] presumably due to the size of the phosphorus ligand. The shortest Pt–Pt distances are 5.988(5) Å in **I** and 7.777(4) Å in **II** which are far too long to suggest any interactions.[30] The molecules seem to be held together by several fairly short hydrogen bonds to the morpholine oxygen atoms. Compound **Ia** differs from **Ib** by having its shortest contacts to aliphatic hydrogen atoms in an adjacent **Ib** molecule, O1–H23, 2.44 Å, O2–H36, 2.31 Å, and O2–H19, 2.52 Å. All distances from the oxygen atoms in **Ia** to aromatic hydrogen atoms in **Ib** are longer than 2.6 Å. The shortest distances from the oxygen atoms in **Ib** to hydrogen atoms in **Ia** are to aromatic hydrogen atoms, O5–H2(C2), 2.45 Å, O6–H4(C4), 2.31 Å, and O6–H5(C7), 2.53 Å, while all distances to aliphatic hydrogen atoms are longer than 2.6 Å. In **II** there are fewer obvious contacts, O1–H2(C2), 2.48 Å, O2–H3(C3), 2.56 Å and O3–H5(C7), 2.42 Å, all hydrogen atoms being aromatic as in **Ib**. As observed in *cis-C,C*-[Pt(tpy)(CO)Cl][18] the hydrogen atom linked to C7, H5, seems to be the best candidate for acceptance of electron density. All distances between the nitrogen end of the solvent molecule and any of the carbon atoms in **II** were longer than 3.5 Å suggesting no specific interactions.

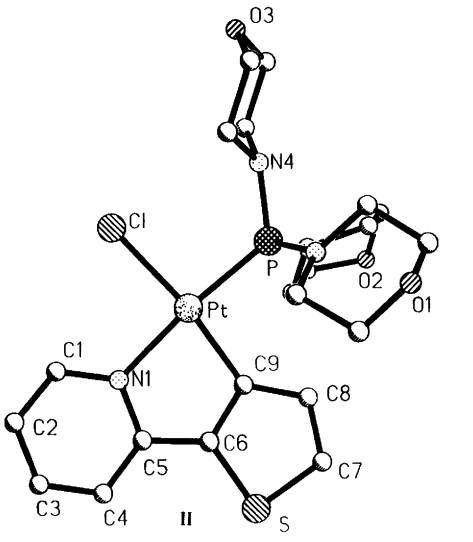
The phosphorus ligand. As shown in structural studies of tris(dialkylamino)phosphines, $(R_2N)_3P$,[22] and of molecules containing this class of tervalent phosphorus species, $(R_2N)_3P$=E (E=S,[31] Se[32] and Te[33]), $(R_2N)_3P$=NC(O)R[34] $(R_2N)_3P$=CH–C(O)R,[35] $(R_2N)_3PFe(CO)_4$ and $(R_2N)_3P)_2Fe(CO)_3$,[36] $[(R_2N)_3P)_2Ag]BPh_4$,[37] *trans-P,P*-$[((R_2N)_3P)_2PtCl_2]$[38] and in some few other compounds[39–41] these molecules are highly asymmetrical with regard to the N–P–N and X–P–N bond angles, the hybridization of the nitrogen atoms and, in some cases, also the P–N bond lengths.[22,31,36–38] This asymmetry with regard to the Pt–P–N and the N–P–N bond angles is also observed in the present compounds. There is one large Pt–P–N bond angle of ca. 120° and two smaller ones, ranging from 110 to 113°. One nitrogen atom in each molecule, N4 (**Ia**), N7 (**Ib**) and N3 (**II**), is slightly



Ia



Ib



II

Fig. 1. Drawings of **Ia**, **Ib** and **II**. The chelating N, C and Pt atoms are in the plane of the paper.

non-planar as viewed by the sum of the bond angles to these atoms, ca. 351°, and its lone pair of electrons is pointing away from the chlorine atom; cf. Fig. 1.

Of particular interest is the sum of the N–P–N bond angles which may serve as a measure for the amount of electron density being transferred from the phosphorus atom to the platinum atom. This sum, ca. 312°, is only some 5° larger than in the parent phosphine, 306.6°,[22] and is considerably less than observed in other derivatives of $(R_2N)_3P$,[31–38] except in $Mn_2(CO)_8[P(NMe_2)_3]_2$,[39] ca. 309°. The slightly pyramidal nature of only one of the nitrogen atoms in each compound and the possible shortening of the P–N bond lengths to ca. 1.675 Å from 1.696, 1.691 and 1.726 Å in the parent phosphine[22] may suggest some P–N π-bonding. A lengthening of the Pt–P bonds due to a concomittant decrease in Pt–P π-bonding,[35] however, is not observed. The upfield ^{31}P shifts displayed by **I** and **II**, 84.3 and 79.2 ppm, from the shift of the parent phosphine, 112.0 ppm, is indicative of some P–N π-interaction.[37]

The Pt–X bond lengths. While the Pt–N bond in $[Pt\langle N\text{–}C\rangle Cl_2)]^-$ is only slightly longer than the Pt–C bond,[23] the Pt–N bond lengths in **I** and **II** are distinctly longer than the Pt–C bond lengths, particularly in **II**. This elongation of the Pt–N bond is as expected from the known *trans* influence of tervalent phosphorus compounds. The longer Pt–N bond in **II** than in **Ia** and **Ib** is probably due to the location of the phosphorus atom close to the plane of the Pt, N and C atoms enabling it to influence the *trans* Pt–N bond more strongly. It is notable that the Pt–Cl bond, 2.388(2) Å in **Ia** [2.385(2) Å in **Ib**] and 2.372(1) Å in **II**, is only slightly shorter than the corresponding bond in $[Pt\langle N\text{–}C\rangle Cl_2]^-$, 2.395(2) Å.[23] This suggests that the *cis* influence[43] by the tervalent phosphorus compound on the Pt–Cl bond length is small.

The aromatic ligands. The *N,C'*-chelated ligands, ppy and tpy, are, as mentioned above, close to being planar, which should favour conjugation between the rings. The lengths of the carbon–carbon bond linking the rings, 1.460(9) Å in **Ia**, 1.467(8) Å in **Ib** and 1.448(6) Å in **II**, are slightly but significantly smaller than 1.49 Å, the accepted bond length for a C–C single bond between two aromatic rings.[44] It is notable that the two C–S bond lengths in **II** are equal; this contrasts the observation for $[Pt(tpy)Cl_2]^-$ in which the C7–S bond length, 1.76(1) Å, was found to be significantly longer than the C6–S bond length, 1.718(7) Å,[23] the latter equal to the C–S bond lengths in **II**.

Electronic spectroscopy. Absorption and emission spectra of **I** and **II** are shown in Figs. 2 and 3. Table 4 contains a list of absorption features for **I** and **II** in various solvents. For comparison the data for $[Pt\langle N\text{–}C\rangle Cl_2]^-$ are also listed. The emission data are summarized in Table 5.

Table 3. Selected bond lengths (in Å) and bond angles (in °) in **Ia** and **II** with estimated standard deviation.

Bond	Ia	II	Angle	Ia	II
Pt–Cl	2.388(2)	2.327(1)	Cl–Pt–P1	90.04(6)[a]	94.72(4)
Pt–P	2.233(2)	2.221(1)	Cl–Pt–N1	90.7(2)	91.4(1)
Pt–N1	2.106(5)	2.134(3)	Cl–Pt–C11(C9)	169.5(2)	171.3(1)
Pt–C11(C9)	2.001(7)	2.017(4)	P–Pt–N1	174.6(2)	173.9(1)
P–N2	1.670(5)	1.674(3)	P–Pt–C11(C9)	98.0(2)[b]	93.9(1)
P–N3	1.663(5)	1.678(3)	N1–Pt–C11(C9)	80.8(2)	80.0(1)
P–N4	1.674(5)	1.680(3)	Pt–N1–C1	126.3(4)	127.2(3)
N1–C1	1.338(8)	1.351(5)	Pt–N1–C5	114.4(4)	113.8(3)
N1–C5	1.366(8)	1.367(5)	C1–N1–C5	119.2(6)	119.1(3)
C5–C6	1.460(9)	1.448(6)	N1–C5–C6	114.2(6)	112.8(3)
C6–C11(C9)	1.431(9)	1.376(5)	C5–C6–C11(C9)	116.6(6)	120.1(4)
C10(C8)–C11(C9)	1.398(9)	1.418(6)	Pt–C11(C9)–C6	114.0(5)	113.3(3)
C6–S		1.715(4)	Pt–C11(C9)–C10(C8)	130.8(5)	136.0(3)
C7–S		1.713(4)	C6–C11(C9)–C10(C8)	115.2(6)	110.7(4)
			C6–S–C7		90.6(2)
			Pt–P–N2	110.7(2)	113.3(2)
			Pt–P–N3	113.0(2)	119.2(2)
			Pt–P–N4	120.3(2)	111.5(2)
			Σ∠N2	356(1)	356(1)
			Σ∠N3	360(1)	351(1)
			Σ∠N4	352(1)	356(1)
			Σ∠NPN[c]	311.7(9)	312.7(6)

[a]93.11(6) Å in **Ib**. [b]96.0(2)° in **Ib**. [c] 306.6° in the parent phosphine; cf. Ref. 22.

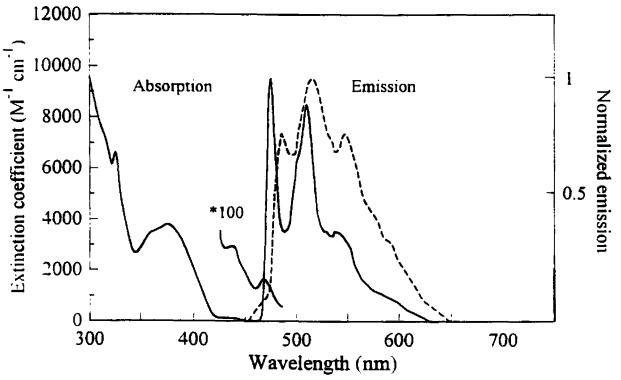


Fig. 2. Room temperature absorption spectrum (left) and the 77 K emission spectra (right) of [Pt(ppy)(Pmor$_3$)Cl], **I**. (Solid line in DMF; dashed line in solid state).

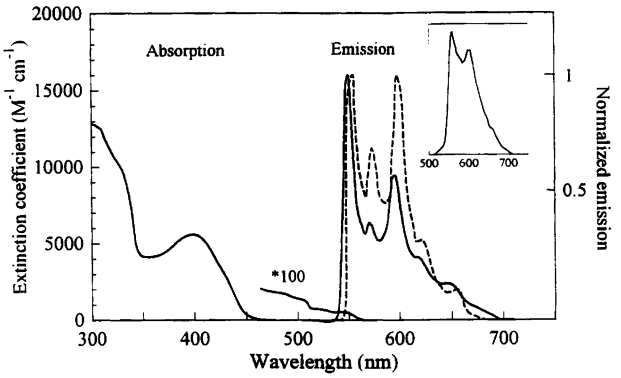


Fig. 3. Room temperature absorption spectrum (left) and the 77 K emission spectra (right) of [Pt(tpy)(Pmor$_3$)Cl], **II**. (Solid line in DMF; dashed line in solid state). Inset: Normalized emission spectrum of **II** in DMF at 298 K.

The absorption and emission spectra of **I** and **II** in solution are in principle quite similar to the previously reported spectra of [Pt⟨N–C⟩Cl$_2$]$^-$ and of other mixed-ligand [Pt⟨N–C⟩AB]^z complexes.[10,11,45,46] The same electronic assignments are therefore suggested. Based on the localized molecular orbital approach the intense absorption bands in the visible and near-UV spectral region, Table 4, are assigned to two types of spin-allowed electronic transitions, one ligand-centered, ^{1}LC, ($\pi_{\langle N-C\rangle} - \pi^*_{\langle N-C\rangle}$) and the other metal-to-ligand charge transfer, ^{1}MLCT, (d_{Pt}–$\pi^*_{\langle N-C\rangle}$). The much weaker but structured absorption in the visible region (Figs. 2 and 3) is attributed to the corresponding spin-forbidden ^{3}MLCT transition. This would be consistent with the modest solvent sensitivity of the long-wave absorption bands (Table 4) and the blue shift of these bands when a π-donor, Cl^-, is replaced by a ligand with π-acceptor properties.

Given the relatively high field strengths of Pmor$_3$ and the *N,C*-chelated ligands, metal-centered ligand field (LF) bands of **I** and **II** are expected to be in the UV region. However, owing to the small extinction coefficients associated with d–d transitions these absorption may be masked by the LC and/or the MLCT bands. The assignment of the lowest energy absorption bands to a ^{3}MLCT transition is substantiated by the long-lived electronic emission. Excitation of **I** and **II** in glassy solutions at 77 K at their low-energy absorption bands (λ_{exc} 330–400 nm) resulted in structured emissions with vibrational progressions of 1000–1500 cm^{-1}, and the electronic origin seems to overlap with the absorption origin, cf. Figs. 2 and 3. The band maxima show modest sensitivity to the solvent as observed for the correspond-

Table 4. Absorption spectra of $[Pt\langle N\text{–}C\rangle Cl_2]^-$ and $[Pt\langle C\text{–}N\rangle(Pmor_3)Cl]$, λ_{max}/nm, $\varepsilon \times 10^{-3}$.

		$^3MLTC(d_{Pt}\text{-}\pi^*_{\langle C\text{–}N\rangle})$		$^1MLTC(d_{Pt}\text{-}\pi^*_{\langle C\text{–}N\rangle})$		LC	
Complex	Solvent	ppy	tpy	ppy	tpy	ppy	tpy
$[Pt\langle C\text{–}N\rangle Cl_2]^-$ [a]	DMF	490(0.058)	565(0.033) 546(0.030) 521(0.05)	380(4.0)[b] 371(4.3)	455(1.7)[b] 428(2.2)	330(4.5)[b]	340(9.0) 298(17.0)
	MeOH	450(0.13)[b]	556(0.027) 536(0.027) 513(0.04)	400(0.8)[b] 365(4.0)	420(2.4) 403(2.6) 360(4.3)	326(5)[b] 314(5)[b]	328(8.5)[b] 300(12.5)[b] 286(13.4)
	CH_2Cl_2	488(0.061)	560(0.028) 538(0.027) 523(0.038) 517(0.040) 497(0.041)[b]	380(4.0)[b] 371(4.3)	440(2.3)[b] 420(2.4) 378(5.1)	330(4.7)	338(9.0)[b] 322(10.5)[b] 307(16.7)[b] 294(16.0)[b]
$[Pt\langle C\text{–}N\rangle(Pmor_3)Cl]$	DMF	470(0.018) 437(0.036)	545(0.011)	376(3.8)	398(5.6)	326(6.8) 315(8.2)[b]	330(11.3)[b] 306(14.1)
	MeOH	469(0.010)		371(3.3)	396(3.9)	325(6.3) 313(7.0)	327(7.6)[b] 304(10.1) 296(9.9)[b]
	CH_3CN	469(0.027) 436(0.039)		373(3.2)	398(4.5)	324(5.9) 312(6.7)[b] 278(15.7)	327(8.7)[b] 305(11.4) 297(11.4)
	CH_2Cl_2	470(0.017) 438(0.029)	546(0.006) 528(0.007)[b] 506(0.012)[b] 484(0.017)[b]	377(3.9)	399(5.8)	326(6.8) 314(8.0)[b] 283(17.1)	330(11.0)[b] 307(14.6) 295(14.0)

[a]From Ref. 45. [b]Shoulder.

Table 5. Luminescence data of $[Pt(ppy)(Pmor_3)Cl]$, **I**, and $[Pt(tpy)(Pmor_3)Cl]$, **II**.

		Solution								Solid	
		293 K				77 K				77 K	
Complex	Solvent	λ_{max}[a]/nm	τ[b]/μs	$\Phi \times 10^b$	τ_r/μs	λ_{max}[a]/nm	τ[b]/μs	$\Phi \times 10^b$	τ_r/μs	λ/nm	τ/μs
I	MeOH	[c]				473	29	3.7	80	486	8.7
	DMF	[c]				476	23	4.0	60		
II	MeOH	555	2.5	0.2	130	548	42	3.1	140	553	42
	DMF	555	2.5	0.1	120	550	42	3.7	110		

[a]Highest energy feature of the luminescence emission maxima. [b]Deareated solution. [c]Emission too weak.

ing MLCT absorption bands. The radiative lifetimes, τ_r, range from 60 to 140 μs (Table 4) and are calculated from the measured emission lifetime, t, and the quantum yield, ϕ. These values are consistent with dipole-allowed spin-forbidden transitions and suggest that there may be some mixing of the LC and MLCT states as proposed for other $[Pt\langle N\text{–}C\rangle AB]^z$ complexes.[11,45] When replacing ppy with tpy a red shift of the MLCT structured absorption and emission bands by ca. 3000 cm^{-1} is observed. The extinction coefficients of **I** are smaller and the radiative lifetimes are longer as compared to the values for **II**. Apparently, the lowest excited state of **II** has a greater contribution of the LC-character of the *N,C'*-chelated ligand as compared to **I**.

Like salts of $[Pt(ppy)Cl_2]^-$ and other $[Pt(ppy)AB]^z$ complexes[11,41] the solution of **I** shows strong emission only at low temperature in rigid media. The emission lifetime and the quantum yield decrease with increasing temperature and no luminescence can be detected at room temperature. This strong temperature quenching of the luminescence can be assigned to the thermally activated population of the upper-lying LF excited states followed by fast radiationless processes. When replacing ppy with tpy the energy of the lowest emitting MLCT excited state is lowered and the energy gap between the emitting and the upper lying LF excited state is increased. As a result compound **II** shows strong emission even at room temperature. The long Pt–Pt internuclear distances preclude Pt–Pt interactions in the ground and excited states in the solid state, and the absence of paralleled coplanar stacking of the aromatic ligands argues against significant π-interactions between adjacent molecular units. Contrary to what is observed for $[Pt(ptpy)(CO)Cl]$[12] the emission spectra of **I** and **II** in glassy solutions at 77 K are therefore unchanged as the concentration of the compounds is increased from 1 μM

to 0.5 mM. Presumably intermolecular interactions are negligible owing to the steric demands of the phosphorous ligand. The solid state emission spectra of **I** and **II**, Figs. 2 and 3, are only slightly perturbed from what is observed in solution. One may therefore conclude that there is small to negligible perturbation of the monomer electronic structure by crystal packing.

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