Spectroscopic and Electrochemical Properties of Cyclometalated Platinum(II) Compounds Containing cis-1,2-Dicyano-1,2-dithiolatoethene

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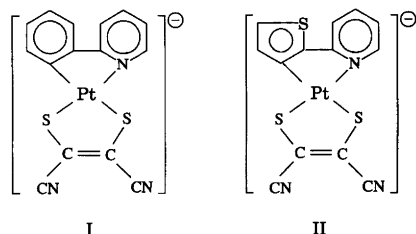
Spectroscopic and electrochemical properties of Bu_4N^+ salts of two $[Pt<N-C>mnt]^-$ ions are reported. $<N-C>$ represents cyclometalated 2-phenylpyridinate, ppy, or 2-(2'-thienyl)pyridinate, tpy, while mnt represents cis-1,2-dicyano-1,2-dithiolatoethene. $Bu_4N[Pt(tpy)mnt]$ is luminescent in fluid solutions with an emission lifetime in DMF of 1.4 µs, whereas $Bu_4N[Pt(ppy)mnt]$ luminesces detectably only in the solid state at room temperature. The electrochemical and spectroscopic results have been compared with available data for a series of Pt(diimine)mnt complexes. The compounds exhibit a dithiolate-centered quasi-reversible one-electron oxidation wave at ca. 0.4 V and a reversible one-electron reduction wave, centered on the cyclometalated ligand, at – 2.4 V vs. Fc^+/Fc. The highly solvatochromic absorption bands are assigned to spin-allowed ligand-to-ligand charge transfer transitions. The energies of these bands show good correlation with the energy gap ($\Delta E_{1/2}$) between the HOMO and LUMO redox orbitals. The lowest-energy spin-forbidden transitions observed in the absorption and emission spectra of the $[Pt<N-C>mnt]^-$ complex ions are attributed to predominantly dithiolate intraligand transitions.

The photochemical and photophysical properties of 4d and particularly 5d metal complexes are known to depend on the orbital nature of the lowest excited state and of the proximity of other excited states. Further knowledge of the nature of these states and the factors determining their relative energies appears to be essential to the development of the chemistry of excited states of this class of compounds. The design of new metal complexes with systematic variation of the donor and acceptor properties of the ligands combined with detailed spectroscopic and voltammetric studies has therefore been the subject of extensive studies in recent years.[1] During the 70s and 80s this research was restricted to octahedral d^6 transition-metal complexes containing heteroaromatic chelating ligands; for leading references see Ref. 2. The observation in the early 80s that also mononuclear square planar d^8 metal complexes could be obtained as luminescent species, even in solution at room temperature,[3–7] has gradually changed the focus of interest toward this class of species.[8–14]

When square-planar metal complexes are the subject of a metal-to-ligand charge-transfer (MLCT) excitation, highly reactive and chemically most interesting 17e metal-centered radicals are formed.[15] Since an increase in the MLCT character of the excited states seems to be connected with increasing covalency of the metal–ligand bonds,[14] platinum(II) species have been the compounds of choice for this type of study.[1,4,5,10,14–28] In most of these systems the lowest emitting states have been assigned to MLCT, $d_{Pt} \rightarrow \pi^*$, transitions. It is not, however, a priori clear whether the first excited states have MLCT or ligand centered (LC) or intraligand, IL, $\pi \rightarrow \pi^*$, character.[14,29] In mixed-ligand complexes an additional complication arises due to the possibility of charge transfer from one ligand to another, LLCT. As has been demonstrated for Pt(α,α'-diimine)(dithiolate) complexes, such LLCT transitions may take place, and may be observed at low energies, when one of the chelated ligands has high-lying filled orbitals and the other has low-lying empty orbitals.[1,9,10,22–31]

von Zelewsky and co-workers[4,5] originally showed that homoleptic cyclometalated Pt^{II} complexes derived from 2-phenylpyridine, ppy, and 2-(2'-thienyl)pyridine, tpy,

Scheme 1.

Fig. 1. Cyclic voltammograms of $Bu_4N[Pt(ppy)mnt]$, I, (———),
$Bu_4N[Pt(tpy)mnt]$, II, (———) and Na_2mnt (— — —) in DMF (a)
and in AN (b).

$[Pt<N-C>_2]$, displayed emissive MLCT excited states.
Much of the later progress in this field has been based
upon this approach.[32,33] Eisenberg[1,22-26] and Vogler[30,31]
with co-workers have studied various $Pt(\alpha,\alpha'$-di-
imine)(dithiolate) complexes and have shown that
chelated dithiolate ligands will favour luminescence
and that the emissive state can be assigned as
$^3\{d\rightarrow\pi^*(dithiolate)\}$.[26] In this work we report on com-
pounds which contain both types of chelating ligands,
$Bu_4N[Pt<N-C>mnt]$, where mnt represents cis-1,2-di-
cyano-1,2-dithiolatoethene; cf. Scheme 1. For compari-
son the electrochemical data for $[Pt<N-C>en]Cl$,[33] en
representing the saturated ligand 1,2-diaminoethane, are
presented.

Experimental

The preparation and characterization of $[Pt<N-C>en]$-
Cl, $Bu_4N[Pt(ppy)mnt]$, I, and $Bu_4N[Pt(tpy)mnt]$, II,
have been described.[34] All solvents were dried and pu-
rified according to standard procedures prior to use. The
salts proved stable in dimethylformamide, DMF, and in
acetonitrile, AN, in which the electrochemical measure-
ments were performed in the presence of 0.1 M
Bu_4NClO_4, TBA.

The instrumentation used has been described.[32,33]

Results and discussion

Electrochemistry. The nature of the HOMO and the
LUMO of the $[Pt<N-C>mnt]^-$ complex ions was ex-
amined using cyclic voltammetry in DMF and AN. From
the cyclic voltammograms, Fig. 1, $E_{1/2}$ values were de-
termined for reversible or quasi-reversible processes
(Table 1).

In a localized molecular orbital approach, reduction
and oxidation of a complex can be classified as metal-
centered or as ligand-centered processes.[35] Previously it
has been shown for a series of mixed-ligand cyclometal-
ated Pt^{II} complexes that oxidation and reduction pro-
cesses involving the metal center exhibit irreversible be-
haviour owing to the instability of the Pt^I and Pt^{III}
states.[32,33] For compounds with cyclometalated aromatic
ligands reduction involves delocalized π^*-orbitals show-
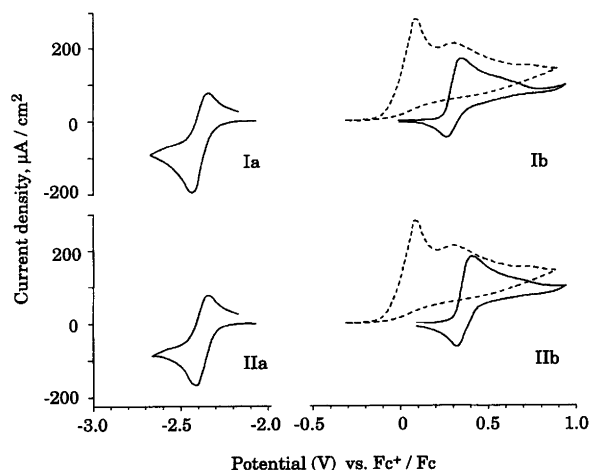ing reversible or a quasi-reversible behaviour, while oxi-

dation is expected to involve a heteroatom and should
exhibit irreversible behaviour. The dithiolate ligand-cen-
tered oxidation process of Pt^{II} complexes, however, is
expected to be quasi-reversible. Extended Hückel mo-
lecular-orbital calculations carried out on a series of
$Pt(\alpha,\alpha'$-diimine)mnt and $Pt(N,N$-diamine)mnt complexes
indicate that one-electron quasi-reversible oxidation of
this type of complexes involves electron transfer from pre-
dominantly sulfur p-orbitals with some delocalization due
to the unsaturated dithiolate ligand.[1]

The results obtained for the $[Pt<N-C>mnt]^-$ com-
plex ions (Table 1) are in agreement with the localized
molecular approach. Compounds I and II show a ligand-
centered reduction wave at $E_{1/2}= -2.40$ and -2.37 V vs.
Fc^+/Fc which can be assigned to electron transfer to the
π^*-orbital localized on the cyclometalated ligand. As
compared to the $[Pt<N-C>en]^+$, complex ions this re-
duction wave for I and II is shifted to a significantly more
negative potential. This is as expected when taking into
account the strong donor properties of the dithiolate
ligand, as exemplified by the large negative Lever poten-
tial value, E_L,[36] of each sulfur atom in the mnt ligand,
-0.33 V,[37] as compared with 0.06 V for en; cf. Ref. 33
for a discussion of the relationship between $E_{1/2}$ and E_L
for square-planar platinum complexes. An increase in the
donation of electrons from the chelated dithiolate ligand
will lead to an increase in the electron density at the metal
center and to a corresponding destabilization of the π^*-
orbital of the cyclometalated ligand. The same LUMO
nature of $[Pt<N-C>mnt]^-$ and of $[Pt<N-C>en]^+$
indicates that the π^*-orbitals localized on the dithiolate
ligand will have higher energy than the π^*-orbitals of the
cyclometalated ligand.

While the reduction processes for $[Pt<N-C>mnt]^-$
and $[Pt<N-C>en]^+$ seem to have similar electronic
origin the character of the oxidation processes of the Pt^{II}
complex ions are distinctly different. Unlike the irrevers-
ible metal-centered two-electron oxidation waves ob-

Table 1. Electrochemical, absorption and emission data for $Bu_4N[Pt<N-C>mnt]$ and $[Pt<N-C>en]Cl$.

	Electrochemistry[a]		Absorption $(T=293$ K)		Electronic spectroscopy[b]				
					Emission				
					$T=293$ K		$T=77$ K		
Complex	Reduction, $-E_{1/2}$ (Δ)	Oxidation, $E_{1/2}$ (Δ)	λ	ε	λ	τ^c	λ	τ	Assignment
$[Pt(ppy)mnt]^-$	2.40 (70)	0.35 (80)	630^d	^{d}	663^d	^{e}	646	^{e}	$(p_S+d_{Pt})\to\pi^*_{mnt}$
$[Pt(tpy)mnt]^-$	2.37 (70)	0.41 (80)	610sh 540	60 140	668	1.4	647	^{e}	$(p_S+d_{Pt})\to\pi^*_{mnt}$ $d_{Pt}\to\pi^*_{tpy}$
$[Pt(ppy)en]^+$	2.22 (75)	0.84^f	477	22	487	1.7	481	15	$d_{Pt}\to\pi^*_{ppy}$
$[Pt(tpy)en]^+$	2.25 (75)	0.86^f	553	6	561	10	556	9	$d_{Pt}\to\pi^*_{tpy}$

^{a} Reduction in DMF and oxidation in AN, in 0.1 M TBA, 293 K, $E_{1/2}$/V vs. Fc^+/Fc, Δ/mV is the difference between the anodic and cathodic waves of the electrochemical process in absolute values. ^{b} Lowest-energy spin-forbidden electronic transitions in DMF; λ in nm, τ in μs. ^{c} Deaerated solution. ^{d} Solid state. ^{e} Non-exponential decay of luminescence. ^{f} Irreversible wave.

served for $[Pt<N-C>en]^+$ and related cyclometalated species,[32,33] and I and II exhibit a one-electron quasi-reversible oxidation wave which is close to the oxidation wave for the free mnt ligand; cf. Fig. 1. This allows us to assign the oxidation process for the two complexes to a dithiolate ligand-centered process. It should be emphasized, however, that in the case of Pt^{II} complexes with a high degree of covalency in the metal–ligand bonds this classification of the redox MO as well as of the excited states, as based on the localized molecular-orbital approach, can only be used as a first approximation. It has been shown for several $Pt(\alpha,\alpha'$-diimine)mnt complexes that the HOMO is predominantly sulfur-p orbitals but with an admixture, ca. 27%, of the metal d-state, giving a partial metal character of the HOMO.[1] A partial metal character of the HOMO for I and II is therefore to be expected.

The obtained electrochemical data show that when the en ligand is replaced by mnt the nature of the redox LUMO, the $\pi^*_{<N-C>}$ orbital localized on the cyclometalated ligand, is not changed. It will, however, lead to a change in the nature of the redox HOMO of the complexes from metal-centered d_{Pt}-orbitals to predominantly dithiolate ligand-centered orbitals with some degree of admixture of the metal state, (p_s+d_{Pt}). This will lead to a change in the nature of the low-energy excited states from MLCT $(d_{Pt}\to\pi^*_{<N-C>})$ to LLCT

Table 2. Low-energy singlet–singlet absorption bands of $[Pt<N-C>mnt]^-$ in solvents of different polarity (ν in 1000 cm^{-1}).

| | $[Pt(ppy)mnt]^-$ | | $[Pt(tpy)mnt]^-$ | |
Solvent	ν_1	ν_2	ν_1	ν_2
$CH_3OH:H_2O$ (4:1)	24.27	24.27	24.30	24.30
CH_3OH	23.3sh	23.98	23.0sh	24.04
CH_3CN	22.83	24.01	22.88	24.04
CH_2Cl_2	22.47	23.98	22.49	23.95
DMF	22.32	23.70	22.35	23.71
$CH_3C_6H_5:C_6H_6:DMF$ (1:1:1)	21.83	23.87	21.85	23.82

$((p_s+d_{Pt})\to\pi^*_{<N-C>})$ and to a change in the absorption and emission properties of the complexes. Moreover, the similar nature of the redox orbitals as well as the low-energy excited states for $[Pt<N-C>mnt]^-$ and $Pt(\alpha,\alpha'$-diimine)mnt complexes allows one to expect a correlation between the energy gap given by $\Delta E_{1,2}$, $\Delta E_{1,2}=E^{ox}-E^{red}$, and the energy of the corresponding long-wave LLCT absorption band.

Absorption and emission data. The Bu_4N^+ salts of the two $[Pt<N-C>mnt]^-$ anions are highly coloured in the solid state. Their absorption spectra are similar and show several intense bands; cf. Fig. 2. As expected from the electrochemical data the absorption bands differ markedly from those of the $[Pt<N-C>en]^+$ ions, the most remarkable feature being the appearance of two new intense bands in the visible region with a significant solvent dependence. The solvatochromic range for the lower-energy band, ν_1, is considerable larger than for ν_2, which clearly indicates that the two low-energy bands of I and II can be assigned to charge-transfer electronic transi-

Fig. 2. Absorption spectra in DMF (———) and diffuse reflectance spectra (— — —) of $Bu_4N[Pt(ppy)mnt]$, upper curves, and of $Bu_4N[Pt(tpy)mnt]$, lower curves ($T=293$ K).

tions with a nature of the excited state being different from that of $[Pt<N-C>en]^+$.[33] Based on the electrochemical data and the solvatochromic effect one may assign the lower-energy absorption band, v_1, to a spin-allowed $(p_s + d_{Pt}) \rightarrow \pi^*_{<N-C>}$ transition which can be classified as being predominantly of the LLCT type. This assignment is supported by the expected correlation between the energy gap, $\Delta E_{1/2}$, and the absorption spectroscopy data for $[Pt<N-C>mnt]^-$ and for a series of related $Pt(\alpha,\alpha'\text{-diimine})mnt$ complexes; cf. Fig. 3.

The assignment of the second low-energy absorption band, v_2, is more complicated owing to the number of possible electronic transitions having charge-transfer character; $d_{Pt} \rightarrow \pi^*_{<N-C>}$, $d_{Pt} \rightarrow \pi^*_{mnt}$ and $(p_s + d_{Pt}) \rightarrow \pi^*_{mnt}$. The electronic transition at ca. 410 nm probably involves the dithiolate moiety, since this absorption is absent in $[Pt(ppy)en]^+$ and in other mixed ligand $[Pt(ppy)(X-X)]^z$ complexes. Intense low-energy absorption bands, $v_{max} = (21-29) \times 10^3$ cm^{-1}, $\varepsilon = (10^3-10^4)$, assigned to a spin-allowed MLCT $d_{Pt} \rightarrow \pi^*_{mnt}$ transition, are present in related dithiolate Pt^{II} complexes like $[Pt(mnt)_2]^{2-}$ and also in PtL_2mnt, where L is $P(Ph)_3$, $P(OPh)_3$ and $P(OEt)_3$ or chelated 1,5-cyclooctadiene and bis(diphenylphosphino)methane.[1,3,38] Thus, the absorption band v_2 of $[Pt(ppy)mnt]^-$, I, can most likely be assigned to a $(p_s + d_{Pt}) \rightarrow \pi^*_{mnt}$ transition with some degree of IL/MLCT character. In the case of $[Pt(tpy)mnt]^-$, II, the broad absorption band at ca. 410 nm probably involves both a $(p_s + d_{Pt}) \rightarrow \pi^*_{mnt}$ and a $d_{Pt} \rightarrow \pi^*_{tpy}$ transition, since related $[Pt(tpy)(X-X)]^z$ complexes exhibit ^{1}MLCT absorption bands between 390 and 430 nm.[33] A ^{1}MLCT $(d_{Pt} \rightarrow \pi^*_{ppy})$ transition of the same nature is also expected for $[Pt(ppy)mnt]^-$ between 360 and 380 nm, but is probably obscured by the intense intraligand $\pi \rightarrow \pi^*_{mnt}$ transition at 341 nm.[32,33]
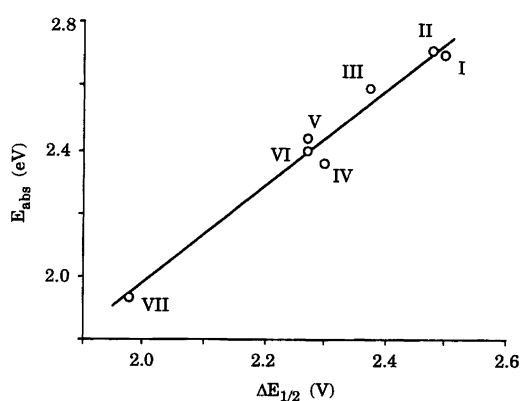
The electrochemical data and the order of the spin-allowed electronic transitions suggest the energy of the π^*-orbitals of the cyclometalated ligand to be lower than that of the π^*-orbitals of the dithiolate ligand. This leads to the following order for the lowest singlet excited states of $[Pt<N-C>mnt]^1$ complexes: ^{1}LLCT $< ^1$(IL/MLCT) $\leq ^1$MLCT.

The absorption curves, Fig. 2, show that the lowest-energy spin-forbidden transitions of I and II appear as shoulders at 610 and 630 nm. Since these transitions do not show notable solvatochromic effect one may rule out the possibility that these absorption features are due to a spin-forbidden component of the LLCT transition. It is, however, difficult to distinguish between the two possible assignments for this absorption, a $^3((p_s + d_{Pt}) \rightarrow \pi^*_{mnt})$ or a $^3(d_{Pt} \rightarrow \pi^*_{<N-C>})$ transition. In analogy with $[Pt<N-C>en]^+$ and related $[Pt<N-C>(X-X)]^z$ complexes[32,33] I and II are expected to have the lowest singlet-triplet $(d_{Pt} \rightarrow \pi^*_{<N-C>})$ transitions near 480 and 550 nm. In the case of $[Pt(ppy)mnt]^-$ this weak absorption band is probably obscured by an intense spin-allowed LLCT transition at 440 nm. The presence of an absorption band at 542 nm ($\varepsilon = 130$) in the spectrum of $[Pt(tpy)mnt]^-$ suggests that the lowest-energy transitions at 610 and 630 nm for I and II can be assigned to spin-forbidden IL/MLCT $((p_s + d_{Pt}) \rightarrow \pi^*_{mnt})$ transitions.

The assignment of the lowest-energy triplet excited state of I and II as ^{3}(IL/MLCT) is supported by the emission data. In the solid state the two Pt^{II} complex ions show detectable luminescence at room temperature. At low temperature the solid-state emissions become structured and are accompanied by an increase in the intensity. The electronic origin of the solid-state emission overlaps well with the lowest energy absorption origin of I and II; cf. Fig. 4. The energy and the band shape of the emission spectra are most similar to the previously reported spectra of the related $[Pt(L_1L_2)mnt]^z$ compounds and the
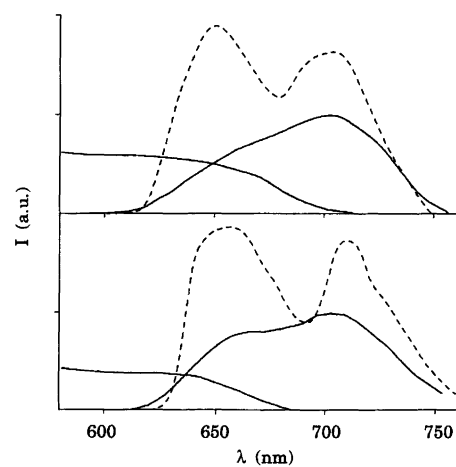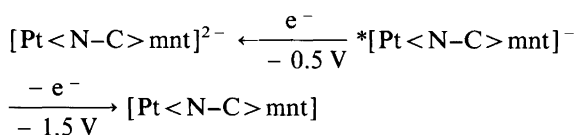

Fig. 3. Plot of the energy gap, $\Delta E_{1/2}$, versus the energy of the LLCT absorption band for $[Pt(ppy)mnt]^-$, I, $[Pt(tpy)mnt]^-$, II, and for related $Pt(\alpha,\alpha'\text{-diimine})mnt$ complexes in AN.[1,10,31] [α,α'-Diimine $=4,4'$-dimethyl-2,2'-bipyridine, III, 1,10-phenantroline, IV, 4,7-diphenyl-1,10-phenantroline, V, 2,2'-bipyridine, VI and N,N-diphenylbut-2-en-2,3-diamine (biacetylbisanyl), VII].

Fig. 4. Solid-state emission and diffuse reflectance spectra of $Bu_4N[Pt(ppy)mnt]$, lower curves, and $Bu_4N[Pt(tpy)mnt]$, upper curves. (——) $T=293$ K; (————) $T=77$ K.

same electronic assignment for the $^3((p_s + d_{Pt}) \rightarrow \pi^*_{mnt})$ transition is suggested.[3,32,33]

[Pt(tpy)mnt]$^-$ shows detectable luminescence in DMF at room temperature. The radiative rate constant is 3×10^3 s^{-1}, as calculated from the measured emission lifetime, 1.4 µs, and the quantum yield, 4×10^{-3}. This value of the radiative rate constant is consistent with a dipole-allowed but spin-forbidden $^3((p_s + d_{Pt}) \rightarrow \pi^*_{mnt})$ transition. The emission from [Pt(ppy)mnt]$^-$ in fluid solution is too weak to be measured, but both **I** and **II** show strong and structured emission at lower temperature; cf. Fig. 5. The emission spectra in DMF are quite similar to the solid-state spectra, but the emission maximum shifts to higher energies by ca. 20 nm. The similarity in the luminescence observed in the solid state and in dilute rigid solution at lower temperatures indicates that the solid-state emission from **I** and **II** is of molecular origin and is not due to dimerization or stacking as observed for other Pt^{II} complexes.[3,39,40] From the absorption and the emission data of **I** and **II** one may therefore conclude that the difference in the singlet–triplet energy splitting for the LLCT, MLCT and IL/MLCT excited states of [Pt<N–C>mnt]$^-$ will lead to different ordering for the singlet and the triplet excited states; for the singlet excited state ^{1}LLCT < ^{1}(IL/MLCT) ≤ ^{1}MLCT and for the triplet excited state ^{3}(IL/MLCT) < ^{3}MLCT, ^{3}LLCT.

Based on the spectroscopic and electrochemical data the excited state redox potentials vs. Fc$^+$/Fc for the [Pt<N–C>mnt]$^-$ complexes can be estimated:

$$[Pt<N-C>mnt]^{2-} \xleftarrow{\ \ e^-\ \ \atop -0.5\,V} {}^*[Pt<N-C>mnt]^-$$

$$\xrightarrow{\ -e^-\ \atop -1.5\,V} [Pt<N-C>mnt]$$

It is apparent from the estimated potentials that the introduction of the mnt ligand in this class of compounds causes a significant decrease in the reduction potential of
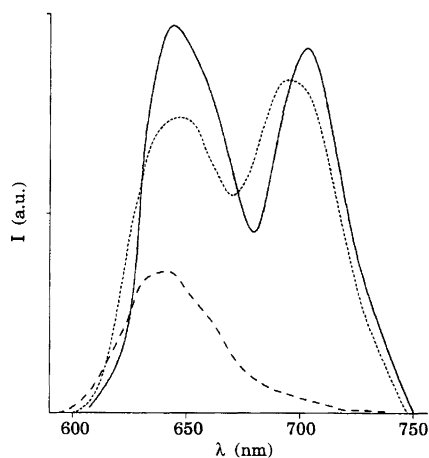
the excited state; for most other [Pt<N–C>AB]^z species the excited-state reduction potentials are positive.[32,33] The oxidation potentials, -1.5 V, are in the range observed for a number of [Pt<N–C>AB]^z species.

The reversible reduction and oxidation behaviour, the excited state energy and the relatively long excited-state lifetime suggest that salts of Pt^{II} complexes that contain both a cyclometalating ligand and a mnt ligand may prove to be useful excited-state reactants for energy- and electron-transfer processes. The salt derived from 2-(2'-thienyl)pyridine, Bu$_4$N[Pt(tpy)mnt], is particularly promising, since it is luminescent at room temperature. The greater luminescent nature of complex species containing the tpy ligand has previously been noted.[33]

References

1. Zuleta, J. A., Bevilacqua, J. M., Proserpio, D. M., Harvey, P. D. and Eisenberg, R. *Inorg. Chem. 31* (1992) 2396.
2. Fox, M. A. and Chanon, M., Eds., *Photoinduced Electron Transfer,* Elsevier, Amsterdam 1989.
3. Johnson, C. E., Eisenberg, R., Evans, T. R. and Burberry, M. S. *J. Am. Chem. Soc. 105* (1983) 1795.
4. Chassot, L., Müller, E. and von Zelewsky, A. *Inorg. Chem. 23* (1984) 4249.
5. Maestri, M., Sandrini, D., Balzani, V., Chassot, L., Jolliet, P. and von Zelewsky, A. *Chem. Phys. Lett. 122* (1985) 375.
6. Fordyce, W. A., Rau, H., Stone, M. L. and Crosby, G. A. *Chem. Phys. Lett. 77* (1981) 405.
7. Fordyce, W. A. and Crosby, G. A. *Inorg. Chem. 21* (1982) 1028.
8. Clanton, C. B. and Rillema, D. P. *Inorg. Chim. Acta 168* (1990) 145.
9. Zuleta, J. A., Chesta, C. A. and Eisenberg, R. *J. Am. Chem. Soc. 111* (1989) 8916.
10. Zuleta, J.A., Burberry, M. S. and Eisenberg, R. *Coord. Chem. Rev. 97* (1990) 47.
11. Maestri, M., Deuschel-Cornioley, C. and von Zelewsky, A. *Coord. Chem. Rev. 111* (1991) 117.
12. Miskowski, V. M. and Houlding, V. H. *Chem. Rev. 111* (1991) 145.
13. Yersin, H., Schützenmeier, S., Wiedenhofer, H. and von Zelewsky, A. *J. Phys. Chem. 97* (1993) 13496.
14. Yersin, H., Huber, P. and Wiedenhofer, H. *Coord. Chem. Rev. 132* (1994) 35.
15. Chan, C.-W., Cheng, L.-K. and Che, C.-M. *Coord. Chem. Rev. 132* (1994) 87.
16. Ballardini, R., Gandolfi, M. T., Prodi, L., Ciano, M., Balzani, V., Kohnke, F. H., Shahriari-Zavareh, H., Spencer, N. and Stoddart, J. F. *J. Am. Chem. Soc. 111* (1989) 7072.
17. Deuschel-Cornioley, C., Lüönd, R. and von Zelewsky, A. *Helv. Chim. Acta 72* (1989) 377.
18. Sandrini, D., Maestri, M., Cianio, M. and Balzani, V. *Gazz. Chim. Ital. 118* (1988) 661.
19. Scolaro, L. M., Alibrandi, G., Romeo, R., Ricevuto, V. and Campagna, S. *Inorg. Chem. 31* (1992) 2074.

Fig. 5. Emission spectra of [Pt<N–C>mnt]$^-$ in DMF. [Pt(ppy)mnt]$^-$: (———) T=77 K; [Pt(tpy)mnt]$^-$: (————) T=77 K; (————) T=293 K.

20. Craig, C. A., Garces, F. O., Watts, R. J., Palmans, R. and Frank, A. J. *Coord. Chem. Rev. 97* (1990) 193.
21. Blanton, C. B., Murtaza, Z., Shaver, R. J. and Rillema, D. P. *Inorg. Chem. 31* (1992) 3230.
22. Zuleta, J. A., Bevilacqua, J. M. and Eisenberg, R. *Coord. Chem. Rev. 111* (1991) 237.
23. Zuleta, J. A., Bevilacqua, J. M., Rehm, J. M. and Eisenberg, R. I. *Inorg. Chem. 31* (1992) 1332.
24. Bevilacqua, J. M., Zuleta, J. A. and Eisenberg, R. *Inorg. Chem. 32* (1993) 3689.
25. Bevilacqua, J. M., Zuleta, J. A. and Eisenberg, R. *Inorg. Chem. 33* (1994) 258.
26. Bevilacqua, J. M. and Eisenberg, R. *Inorg. Chem. 33* (1994) 2913.
27. Chan, C.-W., Lai, T.-F., Che, C.-M. and Peng, S.-M. *J. Am. Chem. Soc. 115* (1993) 11246.
28. Ivanova, M. E. and Shagisultanova G. A. *Russ. J. Inorg. Chem. 36* (1991) 815.
29. Colombo, M. G. and Güdel, H. U. *Inorg. Chem. 32* (1993) 3081.
30. Vogler, A. and Kunkely, H. *J. Am. Chem. Soc. 103* (1981) 1669.
31. Vogler, A., Kunkely, H., Hlavatsch, J. and Merz, A. *Inorg. Chem. 23* (1984) 506.
32. Kvam, P.-I., Puzyk, M. V., Balashev, K. P. and Songstad, J. *Acta Chem. Scand. 49* (1995) 335.
33. Kvam, P.-I., Puzyk, M. V., Cotlyr, V. S., Balashev, K. P. and Songstad, J. *Acta Chem. Scand. 49* (1995) 645.
34. Kvam, P.-I. and Songstad, J. *J. Acta Chem. Scand. 49* (1996) 313.
35. Lees, A. J. *Chem. Rev. 87* (1987) 711.
36. Lever, A. B. P. *Inorg. Chem. 29* (1990) 1271.
37. Greaney, M. A., Coyle, C. L., Harmer, M. A., Jordan, A. and Stiefel, E. I. *Inorg. Chem. 28* (1989) 912.
38. Shupack, S. I., Billig, E., Clark, R. J. H., Williams, R. and Gray, H. B. *J. Am. Chem. Soc. 86* (1964) 4594.
39. Miskowski, V. M. and Houlding, V. H. *Inorg. Chem. 30* (1991) 4446.
40. Houlding, V. H. and Miskowski, V. M. *Coord. Chem. Rev. 111* (1991) 145.