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Exciplex quenching of photoexcited platinum(II) terpyridines: influence of the orbital parentage

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Contents

Abstract

Quenching studies involving a range of Lewis bases establish that exciplex quenching can affect the lifetime of the emissive charge-transfer state of a platinum(II) terpyridine. The

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evidence comes from studies of Pt(trpy)SCN$^+$, where trpy denotes 2,2′:6′,2″-terpyridine, and a Pt(4′-X–T)Cl$^+$ series where 4′-X–T denotes a 4′-substituted trpy derivative and X is a CN, SMe or NMe$_2$ substituent. Thus, in dichloromethane the quenching rate constant increases with the donor number as the quencher varies from a relatively weak base like acetonitrile or acetone to a stronger donor like DMSO or pyridine. For the thiocyanate complex in particular, the quenching rate increases by almost three orders of magnitude. Within the Pt(4′-X–T)Cl$^+$ series, the rates show a marked variation with the electron-donating ability of the substituent X. Thus, with pyridine as the quencher, the rate constant varies from 3.5×10^8 to 1.0×10^{10} M^{-1} s^{-1} as X changes from NMe$_2$ to CN. Variations in the orbital parentage of the excited state account for the trend because the Lewis acidity of the metal center decreases with the delocalization of the hole onto the ligand. When the rate of exciplex formation is slow, an outer-sphere complex accumulates in solution and the kinetic plots show saturation behavior at high quencher concentrations.

Keywords: Exciplex quenching; Platinum(II) terpyridines; Orbital parentage; Charge-transfer states

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1. Introduction

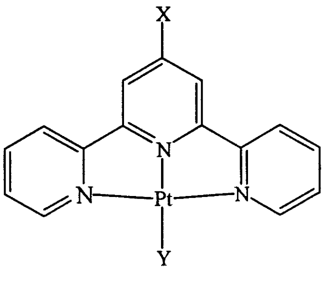
Exciplex formation with Lewis bases can be an important quenching pathway for the excited states of complexes of late transition metal ions [1–4]. With their characteristically high d-electron counts, these metal ions often exhibit relatively low coordination numbers so that ligand addition is a viable reaction for an excited state. The first indication of this type of exciplex quenching came from studies of the reactive metal-to-ligand charge-transfer (CT) excited states of bis-phenanthroline complexes of copper(I) [5]. Subsequent work exploring steric effects provided strong experimental support for the original hypothesis [6,7]. The activation volume of the quenching reaction is often negative, consistent with an increase in the coordination number at the metal center [8]. However, perhaps the most compelling phenomenological evidence of the interaction is the fact that the rate of quenching increases monotonically with the donor strength of the Lewis base [9]. The excited states of d^9 copper(II) porphyrins are also subject to exciplex interactions because Lewis bases are potent quenchers of the π–π* emission from these four-coordinate, quasi-planar complexes in non-coordinating solvents [10–13]. In the case of the porphyrins, conversion to a five-coordinate d–d excited state appears to occur prior to radiationless decay to the ground state [12,13], and even weak bases like acetonitrile are effective quenchers [14].

Here the focus is on the role of exciplex quenching in the photophysics of platinum(II) terpyridines. Axial interactions with Lewis bases are clearly possible with planar platinum(II) systems because in the solid state metal–metal interactions have a profound influence on the chemical and physical properties of columnarly stacked forms [15–18]. Moreover, for the isoelectronic (d^8) nickel(II) porphyrins, flash photolysis studies have demonstrated that a $^3\pi$–π excited state can relax down to the ground state via a d–d excited state with an expanded coordination number [19,20]. To date, however, there is little information available about corresponding interactions in platinum(II) complexes, perhaps because so few systems exhibit photoluminescence in fluid solution [21,22]. Systematic studies of platinum(II) terpyridines could provide useful insights because the complexes can be luminescent, and the use of non-donor media appears to enhance the emission [23]. Furthermore, the lowest energy excited state is likely to be electrophilic because it has substantial metal-to-ligand CT character [21], i.e., the formal charge of the metal center increases in the excited state. Beyond this, an increase in the coordination number becomes more feasible to the degree that the d^7 configuration aptly describes the excited state. The complexes investigated have the generic form $Pt(4'\text{-}X\text{–}T)Y^+$ in Scheme 1 where 4′-X–T denotes a 4′-substituted derivative of 2,2′:6′,2″-terpyridine (trpy) and Y is a halide or pseudo-halide ligand. In all cases Lewis bases act as quenchers, but the kinetics are surprisingly sensitive to the ligand composition.

2. Experimental

2.1. Materials

Aldrich supplied 2,2′:6′,2″-terpyridine, 1,2-difluorobenzene, and ααα-trifluorotoluene. Baxter supplied B&J brand high purity solvents for spectroscopic measurements (acetonitrile, *N*,*N*-dimethylformamide, and dichloromethane). Other solvents were reagent grade. The $K_2[PtCl_4]$ was a gift from Johnson Matthey. In most cases the purity of the materials was satisfactory as received. The [Pt(4′-X–T)Cl]TFPB derivatives and [Pt(trpy)SCN]TFPB were on hand from previous studies [21,23]. (X = CN, SMe or NMe_2, and TFPB denotes the tetrakis[3,5-bis(trifluoromethyl)phenyl]boronate ion.) The laser dyes, Coumarin 440 and Stilbene 420 came from Exciton.



Scheme 1.

2.2. Methods

For steady-state emission measurements, the slit settings were 10 nm for both the excitation and emission beams, and a 400 nm long-wave-pass filter removed the scattered light, where the excitation wavelength was typically 375 nm. For the lifetime studies the excitation wavelength was either 440 or 420 nm, and the cut-off of the long-wave-pass filter was at 475 nm. The concentrations of the Lewis bases (quenchers) varied from submillimolar to several molar in air-saturated solutions according to the strength of the base and the rate of quenching. For the temperature-dependent measurements, the temperature range was from 5 to 40°C. The slope and the intercept of plots of the following equation:

$$\ln\left(\frac{k_q}{T}\right) = \ln\left(\frac{k_B}{h}\right) + \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \tag{1}$$

yielded estimates of the activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$, where k_q is the experimental rate constant for quenching at temperature T, k_B is Boltzmann's constant, h is Planck's constant, and R is the gas constant.

2.3. Instrumentation

The UV–vis spectrophotometer was a Perkin–Elmer Lambda 4C unit, and the spectrofluorometer was an SLM-Amino SPF-500C model. The description of the apparatus for measuring lifetimes is in the literature [24]. The temperature controller was a Brinkmann Instruments model Lauda K-2/RD that circulated a 50/50 (w/w) mixture of water and methanol.

3. Results

3.1. Stability

The absorbance spectra of dilute solutions of the platinum terpyridine complexes are stable in dichloromethane (DCM) for periods of at least hours and usually days. However, during exposure to ambient light, features from the absorption spectrum of the chloride complex $Pt(trpy)Cl^+$ slowly appear in DCM solutions that nominally contain only the thiocyanate complex $Pt(trpy)SCN^+$. The solvent is apparently the source of the chlorine. Overall, the solute stability is no greater in 1,2-difluorobenzene or ααα-trifluoromethylbenzene, hence the solvent of choice has been DCM as it is commercially available in purest form.

3.2. Quenching of $Pt(4'\text{-}X\text{–}T)Cl^+$ complexes

The plots in Fig. 1 indicate that k_q tends to increase with the donor number (DN) of the base, where the DN serves as an all-purpose indicator of the base strength [25]. In the trials the DN varies from 14.1 for the weak base acetonitrile to 33.1 for

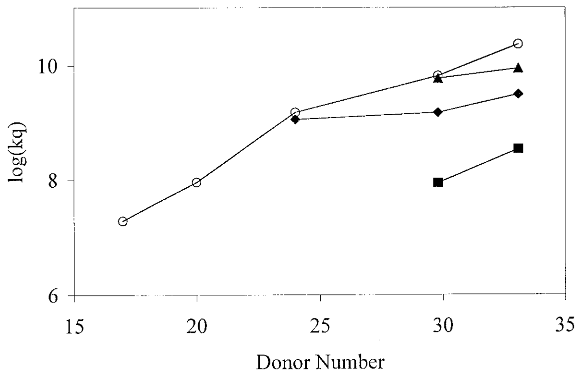


Fig. 1. Quenching rate constants as a function of the donor number of the Lewis base in DCM at 25°C. The symbols correspond to the excited states of: Pt(trpy)SCN$^+$ (○), Pt(4′-CN–T)Cl$^+$ (▲), Pt(4′-SMe–T)Cl$^+$ (◆) and Pt(4′-NMe$_2$–T)Cl$^+$ (■). The lines are simply visual aides. From left to right the bases are acetone, THF, DMF, DMSO and pyridine.

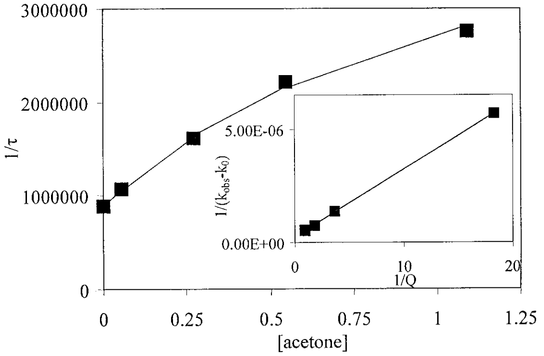


Fig. 2. Decay rate of photoexcited Pt(4′-NMe$_2$–T)Cl$^+$ as a function of acetone concentration in DCM at 25°C. The curve is a plot of Eq. (3) with the parameters from Table 1. Inset: double reciprocal plot of the same data.

pyridine. In general, quenchers with high donor numbers gave linear Stern–Volmer plots, consistent with simple collisionally induced quenching. However, for any given base the quenching constant varies dramatically with the substituent in the 4′ position of the terpyridine ligand. In particular, complexes with an electron-donating group in the 4′ position show substantially lower quenching rates. Thus, with DMSO or pyridine as the quencher, the k_q value of the 4′-CN–T complex is about 30 times higher than that of the 4′-NMe$_2$–T complex and over three times as large as that of the 4′-SMe–T complex (Fig. 1).

For quenchers with low donor numbers, the Stern–Volmer plots tend to exhibit downward curvature, especially for the complex with the 4′-NMe$_2$–T ligand; see Fig. 2 for a representive plot. Downward curvature is a sign of linkage between the quenching step and some type of equilibrium process [3,26–28]. In point of fact, exciplex quenching of the CT state of $Cu(dmp)_2^+$ obeys similar kinetics in the presence of nucleophilic anions, and the quenching rate levels off at higher anion concentrations due to saturation of the ion-pairing equilibrium [29]. In view of the charge on the platinum systems, outer-sphere complex formation with the polar Lewis bases is also likely to occur due to ion–dipole interactions. In keeping with this model, small spectral perturbations are sometimes evident. For example, the emission maximum of the uncorrected spectrum of the 4′-NMe_2–T complex appeared at 540 nm in DCM; however, the maximum shifted to about 545 nm in the presence of molar concentrations of acetonitrile.

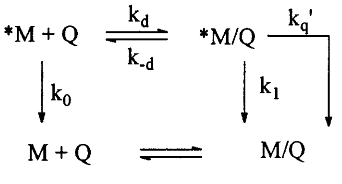
Scheme 2 depicts a minimal reaction sequence. In this model *M/Q represents the outer-sphere complex between the CT state (*M) and a single Lewis base (Q). The net decay rates of *M and *M/Q are k_0 and $k_1 + k'_q$, respectively, where k_0 is the rate constant for decay to the ground in the absence of quencher, k_1 is the corresponding rate constant for the decay of the complex down to the ground state in the absence of inner-sphere complex, i.e. exciplex, formation. The k'_q step accounts for the contribution exciplex formation makes to the decay process. When the decay processes are relatively slow, *M and *M/Q can be in thermal equilibrium; under this assumption, the expression for the observed rate constant for decay is

$$k_{obs} = k_0\left[\frac{N_0}{N_0 + N_1}\right] + (k_1 + k'_q)\left[\frac{N_1}{N_0 + N_1}\right] \tag{2}$$

where N_0 and N_1 represent the amount of *M and *M/Q, respectively, in solution [30]. Once again, in order for this equation to hold, the equilibration steps must be rapid in comparison with the decay rates: k_{-d}, $k_d[Q] > k_0$, $k_1 + k'_q$. If K is the equilibrium constant for formation of the outer-sphere complex, it follows that

$$k_{obs} = \frac{k_0}{1 + K[Q]} + \frac{(k_1 + k'_q)\, K[Q]}{1 + K[Q]} \tag{3}$$

where to a good approximation the concentration of free quencher is equal to the total concentration of quencher. It is possible to determine k_0 independently, but there are three other unknowns in Eq. (2), and Eq. (3) does not permit separate estimates of k_1 and k'_q. However, simplification is possible if outer-sphere complex formation has a minimal influence on the decay of *M. This assumption should be valid unless the outer-sphere interaction significantly alters the excited-state energy, vide infra. In this limit, $k_0 \approx k_1$ and



Scheme 2.

$$k_{\mathrm{obs}} = k_0 + \frac{k'_{\mathrm{q}} K[\mathrm{Q}]}{1 + K[\mathrm{Q}]} \tag{4}$$

Rearrangement of Eq. (4) shows that the intercept of a double-reciprocal plot of $(k_{\mathrm{obs}} - k_0)^{-1}$ versus $[\mathrm{Q}]^{-1}$ yields estimates of k'_{q} and, in conjunction with the slope, K as well. A summary of the values gleaned from such plots appears in Table 1. The interesting trends are that k'_{q} drops off significantly as the 4′ substituent X changes from CN to SMe to $\mathrm{NMe_2}$ and that, for a given platinum complex, the rate constant shows a weak dependence on the donor number.

3.3. *Quenching studies with Pt(trpy)SCN$^+$*

The results for the thiocyanate complex are qualitatively different in that the quenching rate shows a comparatively steep variation with the donor number (Fig. 1). The associated Stern–Volmer plots also show no sign of saturation behavior. In fact, with acetonitrile as the quencher (data not shown), the plot shows slight upward curvature; as though there were a second-order dependence on the quencher concentration. Here, however, the quenching rate is so slow that the emission persists up to acetonitrile concentrations of a few molar. At such high concentrations, however, preferential solvation of the platinum chromophore occurs because the CT absorption maximum shifts about 13 nm toward shorter wavelength. In the face of such wholesale changes in the solute environment, the kinetics model presented above is clearly too simplistic.

3.4. *Temperature studies*

Representative studies of the temperature-dependence of quenching further emphasize the differences in quenching behavior that occur with Pt(trpy)SCN$^+$ and Pt(4′-$\mathrm{NMe_2}$–T)Cl$^+$. For the thiocyanate complex the activation enthalpies for quenching by THF and DMSO are 3 ± 1 and 5 ± 1 kJ mol^{-1}, respectively. The respective entropies of activation are -82 ± 5 and -42 ± 5 J mol^{-1} K^{-1}. In the case of the 4′-$\mathrm{NMe_2}$–T complex, the most meaningful comparisons between bases revolve around the k'_{q} step for which THF and acetone exhibit distinctly higher enthalpies of activation, i.e. 25 ± 10 and 20 ± 10 kJ mol^{-1}, respectively. Note that

Table 1
Results for quenching of Pt(4′-X–T)Cl$^+$ systems by bases of low donor strength

Quencher	DN[a]	X = CN		X = SMe		X = $\mathrm{NMe_2}$	
		k'_{q} (s^{-1})	K (M^{-1})	k'_{q} (s^{-1})	K (M^{-1})	k'_{q} (s^{-1})	K (M^{-1})
MeCN	14.1	2.0×10^8	51	3.3×10^7	1.5	3.3×10^6	3
Acetone	17.0	2.7×10^8	14			5.0×10^6	0.7
EtOH	19.0	2.2×10^8	27	1.7×10^7	5.9		
THF	20.0			2.2×10^7	19	2.1×10^6	10

[a] Ref. [25].

the uncertainties are much greater for the latter estimates due to the added complexity in the kinetics.

4. Discussion

4.1. Comparison with copper(II) porphyrins

The donor-number dependences of the quenching of photoexcited platinum terpyridines are clear indications of exciplex interactions with Lewis bases. Thus, in the case of the Pt(trpy)SCN$^+$ system the k_q value increases by over three orders of magnitude as the quencher ranges from THF to DMSO. This spread in rate exceeds that reported for the Cu(dmp)$_2^+$ system (Fig. 3) [9]. The comparison with Cu(TPP) is even more interesting. Like the porphyrin, the trpy complexes have two open coordination sites, but weak bases are much better quenchers of the copper(II) porphyrin. In assessing the difference in reactivity there are several factors to consider. One is that the metal-to-ligand bonds are relatively strong in square-planar platinum complexes due to the favorable overlap with the 5d$_{x^2-y^2}$ orbital. Consequently, five-coordinate forms of the third-row transition-metal ion may be less accessible. In addition, simple ligand field theory predicts that the barrier against the addition of the fifth ligand will be larger for a d^7 metal than a d^9 system (see, for example, Ref. [31]). Aside from the ligand field parameter Dq, which is larger for the 5d system, the barrier height depends upon the structure of the five-coordinate adduct. One possible structure would be an elongated square pyramid with the added base in the axial position [32]. Alternatively, the five-coordinate platinum terpyridine could exist in two different distorted trigonal bipyramidal structures. In the most obvious structure, the trpy nitrogens reside in the equatorial plane, and there is a considerable elongation of the Pt–Cl or Pt–SCN bond [33]. The other possibility is for the terminal nitrogens of the trpy ligand to

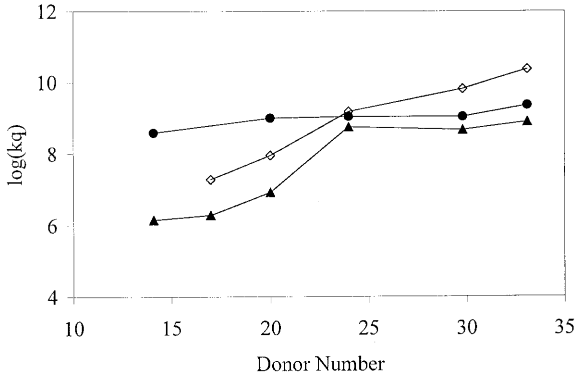


Fig. 3. Exciplex quenching rates as a function of donor number. The symbols denote the excited states of: Cu(dmp)$_2^+$ (▲), Pt(trpy)SCN$^+$ (◇), Cu(TPP) (●). The lines are merely visual aides.

occupy the axial positions of a highly distorted trigonal bipyramid [34]. The above effects may account for the somewhat larger activation energies that one observes for exciplex quenching of platinum terpyridines. (For similar bases, the corresponding numbers for copper(II) porphyrins are 2–10 kJ mol^{-1} [14].) However, another potentially important consideration is the role of the d–d excited states. In the case of the copper(II) porphyrins there is good evidence that the addition of a fifth ligand induces a crossing from the emissive π–π* state to a short-lived d–d state [12,13]. This may result in a threshold effect such that any base capable of inducing the crossing to the d–d state is an excellent quencher. Since the platinum systems have much higher energy d–d excited states, the deactivation is likely to depend solely on direct coupling of the reactive excited state and the ground state surfaces.

4.2. Orbital parentage effects

The profound effects substituents have on the quenching ability for a given base within the Pt(4′-X–T)Cl$^+$ series is a clear sign of a significant electronic effect. Although inductive effects may play some role, the orbital parentage of the emissive state is likely to be the decisive factor as it is in the determination of the intrinsic excited state lifetime [23]. There is widespread agreement that the low-energy absorption bands ($\lambda_{max} \geq 400$ nm) in the visible–near-UV spectra of simple platinum(II) terpyridine complexes have significant metal-to-ligand CT character [21,35], but a proper description of the emissive state must take into account the admixture of other electronic configurations. In addition to platinum-to-trpy charge-transfer character, the low energy excited states of Pt(4′-X–T)Cl$^+$ systems clearly have substituent-to-trpy charge-transfer character which is also a form of π–π*(trpy) excitation [23]. To the extent that there are two competing types of charge transfer, one can formally regard the excited state as a hybrid of two charge distributions:

$$\mathrm{Pt^{II}–T^{-}–X^{+} \leftrightarrow Pt^{III}–T^{-}–X}$$

where the structure on the left designates a pure intraligand CT state and the structure on the right designates a pure MLCT state. Therefore, while the excitation process does tend to create a ‘hole’ in a low-energy metal orbital, the resonance with the other CT configuration provides for significant delocalization of the hole onto the ring substituent. The net effect appears to be mitigation of the electrophilic reactivity of the platinum center in the excited state. The influence of configurational mixing is particularly strong in the case of Pt(4′-NMe$_2$–T)Cl$^+$ which has a remarkably long excited-state lifetime [23]. The same effect will limit the electrophilicity and can account for the sluggishness with which the 4′-NMe$_2$–T system undergoes exciplex quenching. Particularly for the weaker donors, a low k'_q value permits a build up of the outer-sphere complex M*/Q and is ultimately responsible for the observation of unusual saturation kinetics. An alternative possibility is that the excited state is in equilibrium with a relatively long-lived exciplex. However, this explanation is untenable because the shifts in the emission spectrum are too small. With respect to the proposed model, a reviewer has noted that changes in the local solvent environment could alter the mix of configurations that describes the reactive excited state. If this effect were significant, it could jeopardize the $k_0 \approx k_1$ hypothesis.

5. Conclusions

The results described above demonstrate that exciplex formation with a Lewis base can be an important process for the CT excited states of platinum terpyridines. The most convincing evidence is the influence the donor strength has on the rate of quenching. The quenching is relatively efficient when the excited state retains significant MLCT character; however, the introduction of electronically active substituents on the trpy group and/or a change in the nature of the ligand opposite the trpy can significantly alter the kinetics. Most strikingly, electron-donating groups in the 4′ position of the trpy ligand suppress the rate of exciplex quenching due to a change in the orbital parentage of the emissive excited state. For completeness, it is worth noting that the well-known dinuclear platinum system, $Pt_2(pop)_4^{4-}$, takes part in an entirely different type of exciplex formation In the face-to-face platinum dimer, excitation results in the population of a platinum $6p_z$ orbital, which then supports interactions with electron-deficient metal centers [36,37].

Acknowledgements

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References

[1] D.R. McMillin, J.R. Kirchhoff, K.V. Goodwin, Coord. Chem. Rev. 64 (1985) 83.
[2] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.
[3] A. Horváth, K.L. Stevenson, Coord. Chem. Rev. 153 (1996) 57.
[4] D.R. McMillin, K.M. McNett, Chem. Rev. 98 (1998) 1201.
[5] M.W. Blaskie, D.R. McMillin, Inorg. Chem. 19 (1980) 3519.
[6] C.O. Dietrich-Buchecker, P.A. Marnot, J.P. Sauvage, J.R. Kirchhoff, D.R. McMillin, J. Chem. Soc. Chem. Commun. (1983) 513.
[7] M.K. Eggleston, D.R. McMillin, K.S. Koenig, A.J. Pallenberg, Inorg. Chem. 36 (1997) 172.
[8] D.R. Crane, J. DiBenedetto, C.E.A. Palmer, D.R. McMillin, P.C. Ford, Inorg. Chem. 27 (1988) 3698.
[9] E.M. Stacy, D.R. McMillin, Inorg. Chem. 29 (1990) 393.
[10] A. Antipas, D. Dolphin, M. Gouterman, E.C. Johnson, J. Am. Chem. Soc. 100 (1978) 7705.
[11] D. Kim, D. Holten, M. Gouterman, J. Am. Chem. Soc. 106 (1984) 2793.
[12] B.P. Hudson, J. Sou, D.J. Berger, D.R. McMillin, J. Am. Chem. Soc. 114 (1992) 8997.

[13] S.G. Kruglik, P.A. Apanasevich, V.S. Chirvony, V.V. Kvach, V.A. Orlovich, J. Phys. Chem. 99 (1995) 2978.

[14] F. Liu, K.L. Cunningham, W. Uphues, G.W. Fink, J. Schmolt, D.R. McMillin, Inorg. Chem. 34 (1995) 2015.

[15] R. Schwarz, M. Lindner, G. Gilemann, Ber. Bunsenges. Phys. Chem. 91 (1987) 1233.

[16] V.H. Houlding, V.M. Miskowski, Coord. Chem. Rev. 111 (1991) 145.

[17] W.B. Connick, L.M. Henling, R.E. Marsh, H.B. Gray, Inorg. Chem. 35 (1996) 261.

[18] R. Büchner, J.S. Field, R.J. Haines, C.T. Cunningham, D.R. McMillin, Inorg. Chem. 36 (1997) 3952.

[19] D. Kim, D. Holten, Chem. Phys. Lett. 98 (1983) 584.

[20] E.W. Findsen, M.R. Ondrias, J.A. Shelnutt, J.M. Friedman, ACS Symp. Ser. 321 (1986) 266.

[21] T.K. Aldridge, E.M. Stacy, D.R. McMillin, Inorg. Chem. 33 (1994) 722.

[22] S.D. Cummings, R. Eisenberg, J. Am Chem. Soc. 118 (1996) 1949.

[23] D.K. Crites, C.T. Cunningham, D.R. McMillin, Inorg. Chim. Acta 273 (1998) 346.

[24] K.L. Cunningham, C.R. Hecker, D.R. McMillin, Inorg. Chim. Acta 242 (1996) 143.

[25] V. Gutmann, Chimia 31 (1977) 1.

[26] M. Hoshino, H. Seki, H. Shizuka, J. Phys. Chem. 89 (1985) 470.

[27] A. Horváth, K.L. Stevenson, Inorg. Chem. 32 (1993) 2225.

[28] S.M. Hubig, J.K. Kochi, J. Am. Chem. Soc. 121 (1999) 1688.

[29] R.M. Everly, D.R. McMillin, Photochem. Photobiol. 50 (1989) 711.

[30] B. DiBartolo, Optical Interactions in Solids, Wiley, New York, 1968, pp. 442–446.

[31] W.L. Jolly, Modern Inorganic Chemistry, second ed., McGraw-Hill, New York, 1991, pp. 482–494.

[32] R. Cortés, L. Lezama, J.I.R. Larramendi, M. Insausti, J.V. Folgado, G. Madariaga, T. Rojo, J. Chem. Soc. Dalton Trans. (1994) 2573.

[33] A. Kutoglu, R. Allmann, J.V. Folgado, M. Atanasov, D. Reinen, D.Z. Naturforsch. B 46 (1991) 1193.

[34] E.W. Ainscough, A.M. Brodie, S.L. Ingham. J.M. Waters, J. Chem. Soc. Dalton Trans. (1994) 215.

[35] H.K. Yip, L.K. Cheng, K.K. Cheung, C.M. Che, J. Chem. Soc. Dalton Trans. (1993) 2933.

[36] J.K. Nagle, B.A. Brennan, J. Am. Chem. Soc. 110 (1988) 5931.

[37] M.S. Herman, J.L. Goodman, J. Am. Chem. Soc. 111 (1989) 9105.