

Photoinduced isomerisation of *cis*-[M(L-S,O)₂] (M = Pt^{II} and Pd^{II}) complexes of *N,N*-diethyl-*N'*-3,4,5-trimethoxybenzoylthiourea: key to preparation of the *trans* isomer

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In acetonitrile solutions at room temperature, *cis*-[M(L-S,O)₂] Pt^{II} and Pd^{II} complexes of *N,N*-diethyl-*N'*-3,4,5-trimethoxybenzoylthiourea undergo reversible photoinduced isomerisation to the corresponding *trans* isomer upon irradiation with visible light in the 320–570 nm range, the rate and extent of isomerisation being significantly higher for the *cis*-[Pd(L-S,O)₂] complex compared to the Pt^{II} analogue; in the dark *trans*-[M(L-S,O)₂] cleanly reverts back to the *cis* complex at a rate dependent on the solution temperature, indicating a thermally controlled reverse process.

We have in the last decade extensively studied *N,N*-dialkyl-*N'*-aroylthioureas (RRNC(S)NHC(O)R') for their potential analytical and process chemistry applications in the platinum group metals refining industry.¹ These ligands have long been known to readily form stable complexes with softer 1st row transition metal ions as shown from the studies of Hoyer and Beyer² and later König and Schuster.³ Generally these molecules show an overwhelming tendency to coordinate particularly to d⁸ metal ions resulting, upon loss of a proton, in a *cis*-S,O mode of coordination. We have exploited the favorable physicochemical properties of *N,N*-dialkyl-*N'*-acylthioureas (HL) for the convenient reversed-phase high performance liquid chromatographic (*rp*-HPLC) determination of Pt^{II}, Pd^{II} and Rh^{III} in acid chloride media.⁴ Several years ago we serendipitously isolated a first example of a *trans*-bis(*N,N*-di(*n*-butyl)-*N'*-naphthoylthioureato)-platinum(II) complex in ca. 15% yield.⁵ This is one of only two examples of *trans* complexes with these ligands of the more than 25 related crystal structures reported in the Cambridge Structural Database.⁶ Despite considerable effort we have not been able to predictably prepare substantial quantities of *trans*-[Pt(L-S,O)₂] or *trans*-[Pd(L-S,O)₂] complexes with *N,N*-dialkyl-*N'*-aroylthioureas by any standard synthetic route.

We here report that the key to obtaining *trans*-[M(L-S,O)₂] complexes is a photoinduced isomerisation of the *cis*-[M(L¹-S,O)₂] complexes in acetonitrile solution⁷ as monitored by *rp*-HPLC (M = Pt^{II}, Pd^{II} and *N,N*-diethyl-*N'*-3,4,5-trimethoxybenzoylthiourea (HL¹)). Repeated injection of freshly prepared solutions (200 μg cm⁻³) of authentic *cis*-[Pt(L¹-S,O)₂] in MeCN at room temperature, which are kept in the dark over a period of several weeks, show the elution of only a single peak (*t*_R ~ 10.5 min). Identical solutions of *cis*-[Pt(L¹-S,O)₂] exposed to ambient daylight show the development of a second peak in the chromatogram within ca. 30–60 min of exposure, reaching a

steady state within 25 h. As shown for *cis*-[Pt(L¹-S,O)₂] in Fig. 1, the area of the second peak at *t*_R ~ 8.6 min grows with length of exposure to light, while the major peak area correspondingly decreases, eventually reaching a steady state. The absorbance profiles of the two eluted species as obtained by a diode array photometric detector are virtually identical (*λ*_{max} = 307 nm), suggesting that the two peaks are due to *cis*-*trans* isomers. Moreover *rp*-HPLC coupled to electrospray mass spectrometry (ESMS) shows that the two peaks in the chromatogram of *cis*-[Pt(L¹-S,O)₂] solutions exposed to light have the same values (*m/z* 846.83 and 846.57, *calc.* for [C₃₀H₄₂N₄O₈PtS₂·H]⁺ ≈ 846.22), confirming that the smaller peak corresponds to the *trans*-[Pt(L¹-S,O)₂] complex. Fig. 1 shows the peak area ratio *K*_c = [*trans*]/[*cis*] as a function of the time exposed to ambient light at room temperature. Similar observation can be made for *cis*-[Pd(L¹-S,O)₂], although the appearance of the second peak occurs much sooner, and steady state is reached within ca. 1 h.

Experiments show that the rate of photoisomerisation observed for *cis*-[Pt(Lⁿ-S,O)₂] or *cis*-[Pd(Lⁿ-S,O)₂] at room temperature in dilute acetonitrile solutions is significantly influenced by the relative intensity as well as the wavelength range of the light used for irradiation. Irradiation of solutions of *cis*-[Pt(L¹-S,O)₂] or *cis*-[Pd(L¹-S,O)₂] in a water jacketed, 15 cm glass cell using intense white light§ with relatively constant light flux (~320 μmol s⁻¹ m⁻²), results in isomerisation of *cis*-[Pt(L¹-S,O)₂] to a steady state within ca. 70 min (*K*_c = 0.14 ± 0.005), while *cis*-[Pd(L¹-S,O)₂] reaches a steady state within ca. 21 min (*K*_c = 0.43 ± 0.02). The relatively higher rate of isomerisation for *cis*-[Pd(L¹-S,O)₂] complexes at constant photon flux is consistent with the fact that Pd^{II} complexes

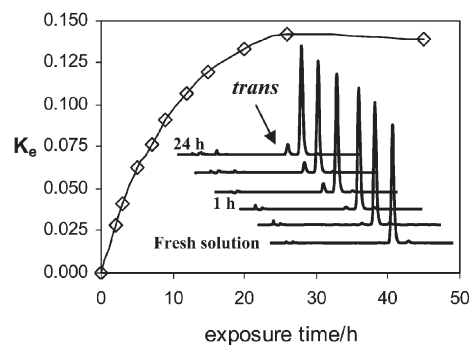


Fig. 1 *K*_c (ratio of *trans/cis* peak areas) for pure *cis*-[Pt(L¹-S,O)₂] in MeCN (ca. 100 μg cm⁻³), as a function of the time exposed to ambient daylight at 20 °C, as monitored by *rp*-HPLC. The inset shows typical chromatograms obtained. Control dark experiments show only one peak.

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are generally more kinetically labile compared to those of Pt^{II}. Experiments using optical filters to yield blue, yellow and red light respectively, show that light in the wavelength range of 320–570 nm is responsible for the observed photoisomerisation. Fig. 2 shows the influence of the wavelength range of visible light on the relative K_e values of *cis*-[Pd(L¹-S,O)₂] being 0.43 ± 0.02 , 0.40 ± 0.05 , 0.20 ± 0.01 and 0.01 for white, blue, yellow and red light respectively.

When the (yellow) light intensity is increased from ~ 320 to $2280 \mu\text{mol s}^{-1} \text{m}^{-2}$, the K_e value increases from 0.20 to 0.40, at 20 °C for *cis*-[Pd(L¹-S,O)₂]. Similar trends are obtained for *cis*-[Pt(L¹-S,O)₂] in MeCN, showing relative K_e values of 0.14 ± 0.01 , 0.10 ± 0.01 , and 0 for white (and blue), yellow and red light respectively. These experiments confirm that *cis*-[M(L¹-S,O)₂] (M = Pt^{II}, Pd^{II}) in solution undergo wavelength dependent photoinduced *cis*–*trans* isomerisation in MeCN. In the absence of light the isomerisation is reversed resulting in pure *cis*-[M(L¹-S,O)₂] again, suggesting a thermally controlled reverse reaction.

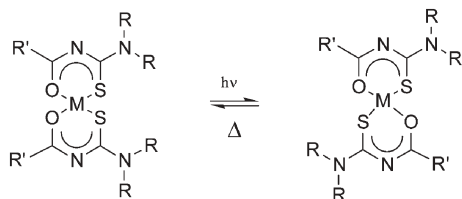


Fig. 3 clearly shows that K_e is temperature dependent, and that after an appropriate time in the dark, only the *cis* complex is again found in solution as monitored by *rp*-HPLC. Monitoring the isomerisation by *rp*-HPLC has the disadvantage of a time delay corresponding to the retention-time of the complexes on column. Thus monitoring the reverse *trans* to *cis* thermal reaction of *inter alia* *cis*-[Pd(L¹-S,O)₂] after irradiation with white light at various temperatures by means of ¹H NMR, confirms the results obtained with *rp*-HPLC. Fig. 4 shows a typical series of ¹H NMR spectra as a function of time after irradiation, confirming that the resonance at $\delta \sim 7.33$ ppm (assigned to H2 and H6 of the trimethoxybenzoyl moiety) due to the *trans* complex decreases with time and the $\delta \sim 7.53$ ppm resonance of the *cis* isomer grows to eventually dominate the spectrum again.

In conclusion, although photoinduced geometrical isomerisations of metal complexes particularly with monodentate ligands

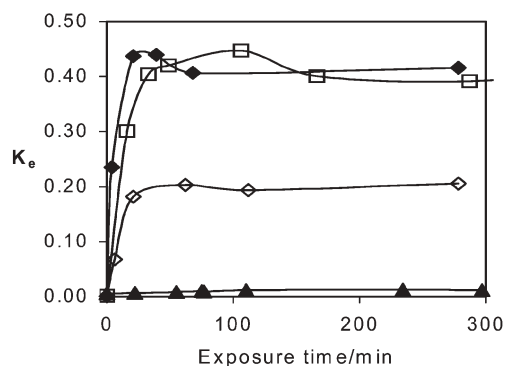


Fig. 2 K_e for pure *cis*-[Pd(L¹-S,O)₂] in MeCN (20 °C) as a function of wavelength of irradiation at relatively constant intensity. □ white; ◆ blue (cutoff 310 nm); ◇ yellow (465 nm); ▲ red (580 nm) light.

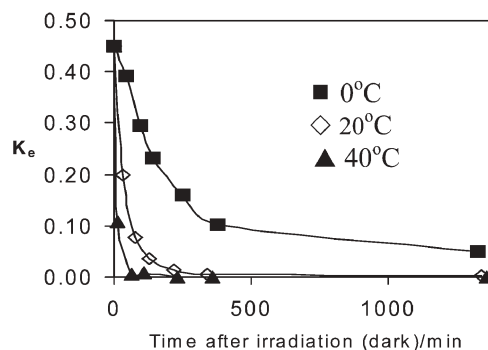


Fig. 3 K_e for ca. $200 \mu\text{g cm}^{-3}$ *cis*-[Pd(L¹-S,O)₂] in MeCN kept in the dark after irradiation at relatively constant intensity with white light as a function of temperature, as monitored by *rp*-HPLC.

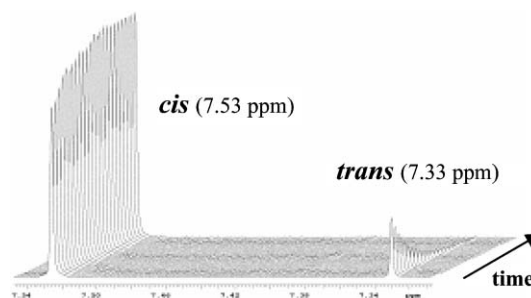


Fig. 4 Expanded ¹H NMR spectra of *cis*-[Pd(L¹-S,O)₂] in MeCN at 20 °C in the dark, showing a *trans* to *cis* isomerisation after irradiation with white light to steady state; ¹H(2,6) trimethoxyphenyl resonances.

are known,⁸ such geometrical isomerisations are rare for chelating ligands, and there is to our knowledge only one well-studied case of a photoinduced *cis*–*trans* isomerisation observed for the [Pt(glycinato)₂] complex in the literature,⁸ with no examples of comparable Pd^{II} complexes. The well studied facile *cis*–*trans* isomerism of bis(glycinato)copper(II) complexes,⁹ is apparently *not* photoinduced, occurring spontaneously at ambient temperatures, presumably *via* an energetically favourable ring-twisting mechanism.¹⁰ We are currently investigating in detail the possible mechanisms of the photoisomerisation of *cis*-[M(L-S,O)₂] reported here.

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Notes and references

† Ligands HL¹, and the corresponding *cis*-[M(L¹-S,O)₂] complexes (M = Pt^{II}, Pd^{II}) were prepared as previously described,^{1,4} fully characterised by elemental analysis, mp and ¹H and ¹³C NMR in CDCl₃; *cis*-[Pt(L¹-S,O)₂] was confirmed by single crystal X-ray diffraction (unpublished results; K. R. Koch, J. Miller and L. Barbour, 2003).

‡ *rp*-HPLC conditions: 150 mm × 4.6 mm, Luna (end-capped) 5 μm C18 column, isocratic flow at 1 cm³ min⁻¹, mobile phase: 90% CH₃CN, 10% 0.1 M sodium acetate buffer pH 6, 20 μL injections, photometric detection.

§ Light source 150 W quartz-halogen lamp from a conventional slide projector; intensity measured with an LI-250 quantum meter (Lincoln, LI-COR, USA). Photographic optical filters blue (80B), yellow (Y2) and red (25A) provided coloured light.

- 1 K. R. Koch, *Coord. Chem. Rev.*, 2001, **216**, 473; K. R. Koch, C. Sacht, T. Grimmacher and S. Bourne, *S. Afr. J. Chem.*, 1995, **48**, 71.
- 2 L. Beyer, E. Hoyer, H. Hartman and J. Liebscher, *Z. Chem.*, 1981, **21**, 81; P. Mühl, K. Gloe, F. Dietze, E. Hoyer and L. Beyer, *Z. Chem.*, 1986, **26**, 81.
- 3 K.-H. König, M. Schuster, B. Steinbrech, G. Schneeweis and R. Schlodder, *Fresenius' Z. Anal. Chem.*, 1985, **321**, 457; K.-H. König, M. Schuster, G. Schneeweis and B. Steinbrech, *Fresenius' Z. Anal. Chem.*, 1984, **319**, 66; M. Schuster, *Fresenius' Z. Anal. Chem.*, 1992, **342**, 791; M. Schuster and M. Schwarzer, *Anal. Chim. Acta*, 1996, **328**, 1; M. Schuster and M. Sandor, *Fresenius' Z. Anal. Chem.*, 1996, **356**, 326.
- 4 A. N. Mautjana, J. D. Miller, A. Gie, S. A. Bourne and K. R. Koch, *J. Chem. Soc., Dalton Trans.*, 2003, 1952.
- 5 K. R. Koch, J. du Toit, M. R. Cairra and C. Sacht, *J. Chem. Soc., Dalton Trans.*, 1994, 785.
- 6 F. H. Allen, *Acta Crystallogr., Sect. B*, 2002, **58**, 380–388 CSC Version 5.25 updates (Jul 2004).
- 7 D. Hanekom and K. R. Koch, Presented in part as poster at the 36th International Conference on Coordination Chemistry, Merida, Mexico, 18–23 July, 2004. (Best poster in section award).
- 8 F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini and V. Carassiti, *Inorg. Chim. Acta*, 1967, **1**, 76; C. R. Bock and A. E. Koerner von Gustorf, in *Advances in Photochemistry*, eds. J. N. Pitts, G. S. Hammond and K. Gollnick, Interscience Publication, John Wiley & Sons, New York, 1977, vol. 10, pp. 221–310.
- 9 P. O'Brien, *J. Chem. Educ.*, 1982, **59**, 1052–1053; S. M. Moussa, R. R. Fenton, B. A. Hunter and B. J. Kennedy, *Aust. J. Chem.*, 2002, **55**, 3319.
- 10 C. S. Trautermann, J. Sabolović, A. F. Voegelé and K. R. Liedl, *J. Phys. Chem.*, 2004, **108**, 2098.