## Photoinduced isomerisation of cis-[M(L-S,O)<sub>2</sub>] (M = Pt<sup>II</sup> and Pd<sup>II</sup>) 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)<sub>2</sub>] Pt<sup>II</sup> and Pd<sup>II</sup> 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*)<sub>2</sub>] complex compared to the Pt<sup>II</sup> analogue; in the dark *trans*-[M(L-*S*,*O*)<sub>2</sub>] 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.<sup>1</sup> 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 Beyer<sup>2</sup> and later König and Schuster.<sup>3</sup> Generally these molecules show an overwhelming tendency to coordinate particularly to d<sup>8</sup> metal ions resulting, upon loss of a proton, in a cis-S,O mode of coordination. We have exploited the favorable physiochemical properties of N,N-dialkyl-N'-acylthioureas (HL) for the convenient reversed-phase high performance liquid chromatographic (rp-HPLC) determination of Pt<sup>II</sup>, Pd<sup>II</sup> and Rh<sup>III</sup> in acid chloride media.<sup>4</sup> Several years ago we serendipidously isolated a first example of a trans-bis(N,N-di(n-butyl)-N'-naphthoylthioureato)platinum(II) complex in ca. 15% yield.<sup>5</sup> 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.<sup>6</sup> Despite considerable effort we have not been able to predictably prepare substantial quantities of trans-[Pt(L-S,O)<sub>2</sub>] 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*)<sub>2</sub>] complexes is a photoinduced isomerisation of the *cis*-[M(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] complexes in acetonitrile solution<sup>7</sup> as monitored by *rp*-HPLC (M = Pt<sup>II</sup>, Pd<sup>II</sup> and *N*,*N*-diethyl-*N'*-3,4,5-trimethoxyben-zoylthiourea (HL<sup>1</sup>))†. Repeated injection of freshly prepared solutions (200 µg cm<sup>-3</sup>) of authentic *cis*-[Pt(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] 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 ( $t_{\rm R} \sim 10.5 \text{ min}$ )‡. Identical solutions of *cis*-[Pt(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] 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(L<sup>1</sup>-S,O)<sub>2</sub>] in Fig. 1, the area of the second peak at  $t_{\rm R} \sim 8.6$  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 ( $\lambda_{max} = 307$  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- $[Pt(L^1-S,O)_2]$  solutions exposed to light have the same values (m/z)846.83 and 846.57, *calc.* for  $[C_{30}H_{42}N_4O_8PtS_2 \cdot H]^+ \approx 846.22)$ , confirming that the smaller peak corresponds to the trans-[Pt(L1- $(S,O)_2$  complex. Fig. 1 shows the peak area ratio  $K_e = [trans]/[cis]$ 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(L<sup>*n*</sup>-*S*,*O*)<sub>2</sub>] or *cis*-[Pd(L<sup>*n*</sup>-*S*,*O*)<sub>2</sub>] 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(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] or *cis*-[Pd(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] in a water jacketed, 15 cm glass cell using intense white light§ with relatively constant light flux (~ 320 µmol s<sup>-1</sup> m<sup>-2</sup>), results in isomerisation of *cis*-[Pt(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] to a steady state within *ca*. 70 min ( $K_e = 0.14 \pm 0.005$ ), while *cis*-[Pd(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] reaches a steady state within *ca*. 21 min ( $K_e = 0.43 \pm 0.02$ ). The relatively higher rate of isomerisation for *cis*-[Pd(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] complexes at constant photon flux is consistent with the fact that Pd<sup>II</sup> complexes



**Fig. 1**  $K_e$  (ratio of *translcis* peak areas) for pure *cis*-[Pt(L<sup>1</sup>-*S*, *O*)<sub>2</sub>] in MeCN (*ca.* 100 µg cm<sup>-3</sup>), 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<sup>II</sup>. 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(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] being 0.43  $\pm$  0.02, 0.40  $\pm$  0.05, 0.20  $\pm$  0.01 and 0.01 for white, blue, yellow and red light respectively.

When the (yellow) light intensity is increased from ~ 320 to 2280 µmol s<sup>-1</sup> m<sup>-2</sup>, the  $K_e$  value increases from 0.20 to 0.40, at 20 °C for *cis*-[Pd(L<sup>1</sup>-*S*,*O*)<sub>2</sub>]. Similar trends are obtained for *cis*-[Pt(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] 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(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] (M = Pt<sup>II</sup>, Pd<sup>II</sup>) 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(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] 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(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] after irradiation with white light at various temperatures by means of <sup>1</sup>H NMR, confirms the results obtained with *rp*-HPLC. Fig. 4 shows a typical series of <sup>1</sup>H 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 isomerizations of metal complexes particularly with monodentate ligands



**Fig. 2**  $K_e$  for pure *cis*-[Pd(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] in MeCN (20 °C) as a function of wavelength of irradiation at relatively constant intensity.  $\Box$  white;  $\blacklozenge$  blue (cutoff 310 nm);  $\diamondsuit$  yellow (465 nm);  $\blacktriangle$  red (580 nm) light.



**Fig. 3**  $K_e$  for *ca.* 200 µg cm<sup>-3</sup> *cis*-[Pd(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] 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 <sup>1</sup>H NMR spectra of *cis*-[Pd( $L^{1}$ -*S*,*O*)<sub>2</sub>] in MeCN at 20 °C in the dark, showing a *trans* to *cis* isomerisation after irradiation with white light to steady state; <sup>1</sup>H(2,6) trimethoxyphenyl resonances.

are known,<sup>8</sup> 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,<sup>8</sup> with no examples of comparable Pd<sup>II</sup> complexes. The well studied facile *cis–trans* isomerism of bis(glycinato)copper(II) complexes,<sup>9</sup> is apparently *not* photoinduced, occurring spontaneously at ambient temperatures, presumably *via* an energetically favourable ring-twisting mechanism.<sup>10</sup> 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

<sup>†</sup> Ligands **HL**<sup>1</sup>, and the corresponding *cis*-[M(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] complexes (M = Pt<sup>II</sup>, Pd<sup>II</sup>) were prepared as previously described,<sup>1,4</sup> fully characterised by elemental analysis, mp and <sup>1</sup>H and <sup>13</sup>C NMR in CDCl<sub>3</sub>; *cis*-[Pt(L<sup>1</sup>-*S*,*O*)<sub>2</sub>] was confirmed by single crystal X-ray diffraction (unpublished results; K. R. Koch, J. Miller and L. Barbour, 2003).

 $\ddagger rp$ -HPLC conditions: 150 mm  $\times$  4.6 mm, Luna (end-capped) 5  $\mu$ m C18 column, isocratic flow at 1 cm<sup>3</sup> min<sup>-1</sup>, mobile phase: 90% CH<sub>3</sub>CN, 10% 0.1 M sodium acetate buffer pH 6, 20  $\mu$ L 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.

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