Synthesis and Crystal Structure of *trans*-Bis(*N*,*N*-dibutyl-*N*′-naphthoylthioureato)platinum(II). First Example of *trans* Chelation of *N*,*N*-Dialkyl-*N*′-acylthiourea Ligands

Klaus R. Koch,* Judith du Toit, Mino R. Caira and Cheryl Sacht
Department of Chemistry, University of Cape Town, Private Bag, Rondebosch, 7700, Republic of South Africa

---

N,*N*-Dibutyl-*N*′-naphthoylthiourea (HL^1) reacted with $[PtCl_4]^{2-}$ to yield a mixture of *cis*- (85%) and *trans*-$[PtL^1{}_2]$ (15%); the crystal structure of the latter has been determined and represents the first example of *trans* chelation of *N*,*N*-dialkyl-*N*′-acylthiourea ligands.

The selective binding of *N*,*N*-dialkyl-*N*′-benzoyl- (HL) and *N*-alkyl-*N*′-benzoyl-thioureas (H_2L) to the platinum-group metals has stimulated interest in these ligands.[1–5] We have found that the co-ordination to Pt^{II} of the monoalkyl-substituted ligand differs substantially from the corresponding dialkyl-substituted analogue, in that the former yields a mixture of *cis*- and *trans*-$[Pt(H_2L)_2Cl_2]$ involving unidentate co-ordination *via* the sulfur atom to the metal ion,[5] while the dialkyl-substituted ligands have to date only yielded *cis*-$[ML_2]$, several of which have been isolated and characterized by X-ray diffraction for M = Ni^{II},[6,7] Pd^{II}[8] and Pt^{II}.[4]

As part of our interest in these deceptively simple ligand systems, we have studied the co-ordination of the potentially fluorescent *N*,*N*-dibutyl-*N*′-naphthoylthiourea (HL^1).† We find that treatment of $K_2[PtCl_4]$ with HL^1 ‡ yields a mixture of (85%) *cis*- and (15%) *trans*-$[PtL^1{}_2]$ in sharp contrast to *N*-benzoyl-*N*′,*N*′-dibutylthiourea (HL^2) which only yields *cis*-$[PtL^2{}_2]$, despite efforts to prepare its *trans* analogue.[4]

Here we report the crystal structure§ of the first example of a *trans* complex involving these chelating acylthiourea type ligands. *trans*-Bis(*N*,*N*-dibutyl-*N*′-naphthoylthioureato)platinum(II), *trans*-$[PtL^1{}_2]$, was isolated as the minor component from the mixture by means of fractional crystallization ($CHCl_3$–MeCN, *ca.* 20:80 v/v) as it was not possible to separate these isomers readily by chromatographic means (TLC, silica gel, $CHCl_3$).

The crystal structure of *trans*-$[PtL^1{}_2]$ is shown in Fig. 1, revealing essentially square-planar *O*,*S*-bidentate co-ordination of the ligand to the platinum atom [Pt–S 2.250(4) and Pt–O 1.98(1) Å; S(2)–Pt–O(3B) 85.6(3), S(2)–Pt–O(3) 94.4(4), O(3)–Pt–O(3B) 179.0(6) and S(2)–Pt–S(2B) 179.9(2)°]. The maximum deviation from the least-squares plane through the platinum atom and its four co-ordinating atoms (plane 1) is 0.01(1) Å. By comparison with the structure of the uncomplexed ligand[13] the C=S and C=O bond lengths in *trans*-$[PtL^1{}_2]$ are significantly longer [1.75(2) and 1.28(3) Å, respectively] than those in the free ligand [1.662(2) and 1.215(3) Å, respectively]. Furthermore the corresponding two contiguous C–N bond lengths [C(15)–N(16) and N(16)–C(4)] of the chelate ring are on average shorter in *trans*-$[PtL^1{}_2]$ [1.36(1) and 1.30(2) Å, respectively] as compared to the free ligand [1.420(4) and 1.376(4) Å, respectively]. These changes in the bond lengths upon complexation indicate extensive delocalization of electrons within the chelate ring of the complex, similar to that observed in the analogue *cis*-$[PtL^2{}_2]$.[4] The least-squares plane including atoms C(5)–C(15) (plane 2) was calculated, yielding a maximum deviation from the plane of 0.06(3) Å for atom

---

† HL^1 was prepared according to the method of Douglass and Dains.[9] M.p. 95–99 °C (Found: C, 69.0; H, 6.8; N, 8.0. $C_{20}H_{26}N_2OS$ requires C, 70.2; H, 7.6; N, 8.2%); δ_H(400 MHz, $CDCl_3$) 8.46 (1 H, d, H^8), 8.17 (1 H, s, NH), 8.01 (1 H, d, H^2), 7.90 (1 H, d, H^4), 7.76 (1 H, d, H^5), 7.61 (1 H, t, H^6), 7.56 (1 H, t, H^3), 7.50 (1 H, t, H^7), 4.01 (2 H, t, NCH_2), 3.69 (2 H, t, NCH_2), 1.84 (2 H, t, NCH_2CH_2), 1.74 (2 H, t, NCH_2CH_2), 1.48 (2 H, q, $-CH_2CH_3$), 1.38 (2 H, q, $-CH_2CH_3$), 1.01 (3 H, t, $-CH_3$), 0.98 (3 H, t, $-CH_3$).

‡ A solution of $K_2[PtCl_4]$ (45.7 mg, 0.1098 mmol) in H_2O–dioxane (1:1 v/v) was added slowly to a warm (50 °C) solution of HL^1 (75 mg, 0.219 mmol) in dioxane (20 cm^3)–H_2O (10 cm^3). The solution was allowed to stir for a further 30 min at 50 °C. Upon cooling, excess water was added and the bright yellow precipitate obtained was collected by filtration in virtually quantitative yield. The crude product was taken up in chloroform and washed with dilute (0.05 mol dm^{-3}) NaOH to ensure complete deprotonation of the complexed ligand. The organic phase was separated, dried over Na_2SO_4 and evaporated to dryness to yield $[PtL^1{}_2]$. The relative amounts of *cis*- and *trans*-isomers of the complex were estimated from the ^{1}H NMR resonance intensities of analytically pure, unrecrystallized $[PtL^1{}_2]$. M.p. 110–113 °C, TLC (silica gel) $R_f(CHCl_3) = 0.88$ (Found: C, 54.8; H, 4.1; N, 6.2. $C_{40}H_{50}N_4O_2PtS_2$ requires C, 54.7; H, 5.7; N, 6.4%); δ_H(400 MHz, $CDCl_3$) *cis*-$[PtL^1{}_2]$: 8.94 (1 H, d, H^8), 8.15 (2 H, d, H^2), 7.91 (2 H, d, H^4), 7.81 (2 H, d, H^5), 7.44 (2 H, t, H^3), 7.36 (2 H, t, H^6), 7.09 (2 H, t, H^7), 3.73 (4 H, t, $2NCH_2$), 1.80 (2 H, q, NCH_2CH_2), 1.69 (2 H, q, NCH_2CH_2), 1.45 (2 H, q, $-CH_2CH_3$), 1.34 (2 H, q, $-CH_2CH_3$), 1.01 (3 H, t, $-CH_3$), 0.91 (3 H, t, $-CH_3$); *trans*-$[PtL^1{}_2]$: 8.61 (1 H, d, H^8), 7.95 (1 H, d, H^2), 7.91 (1 H, d, H^4), 7.84 (1 H, d, H^5), 7.55 (1 H, t, H^7), 7.47 (1 H, t, H^6), 7.42 (1 H, t, H^3), 3.73 (4 H, t, $2NCH_2$), 1.82 (2 H, q, NCH_2CH_2), 1.68 (2 H, q, NCH_2CH_2), 1.40 (2 H, q, $-CH_2CH_3$), 1.31 (2 H, q, $-CH_2CH_3$), 0.97 (3 H, t, $-CH_3$), 0.89 (3 H, t, $-CH_3$).

§ Crystal data: $C_{40}H_{50}N_4O_2PtS_2$, yellow crystal, 0.25 × 0.25 × 0.13 mm, $M = 878.07$, hexagonal, space group $P6_4$ (no. 172), $a = 16.690(2)$, $c = 12.308(3)$ Å, $U = 2969(1)$ Å^3, $Z = 3$, $D_c = 1.473$ g cm^{-3}, $F(000) = 1332$, μ(Mo-Kα) = 37.2 cm^{-1}. A total of 2037 reflection intensities were collected in the θ range 1–25° on an Enraf-Nonius CAD4 diffractometer with Mo-Kα radiation (λ = 0.710 69 Å) at 294 K using the ω–2θ scan technique. Lorentz-polarisation and empirical absorption corrections were applied. The space group requires the Pt atom to lie on a two-fold axis. The structure was solved by locating the Pt and S atoms using Patterson vector methods with SHELX 86.[10] The remaining atoms were located in subsequent ΔF maps. Full-matrix least-squares refinement treating the non-hydrogen atoms anisotropically was performed with SHELX 76[11] using 1376 reflections having $I > \sigma(I)$. No H atoms were included in the model. Final refinement converged at $R = 0.046$. The absolute structure ($P6_4$ rather than the enantiomorphous space group $P6_2$) was assigned on the basis of the Flack x parameter calculated using SHELXL 93.[12] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

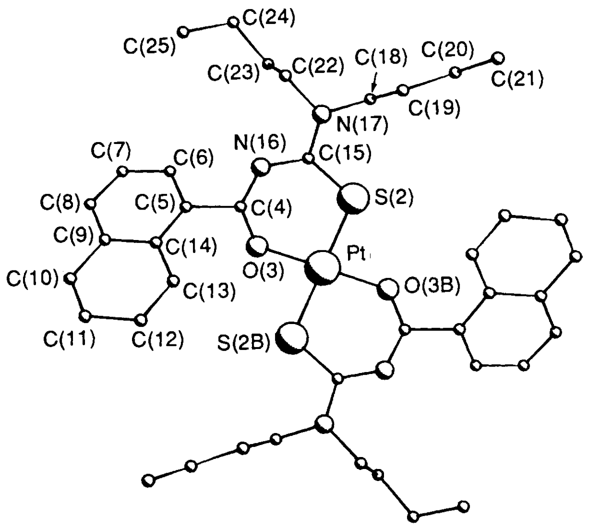

Fig. 1 Molecular structure of *trans*-bis(*N*,*N*-dibutyl-*N*′-naphthoylthioureato)platinum(II) showing the numbering scheme adopted (see text for significant bond lengths and angles)

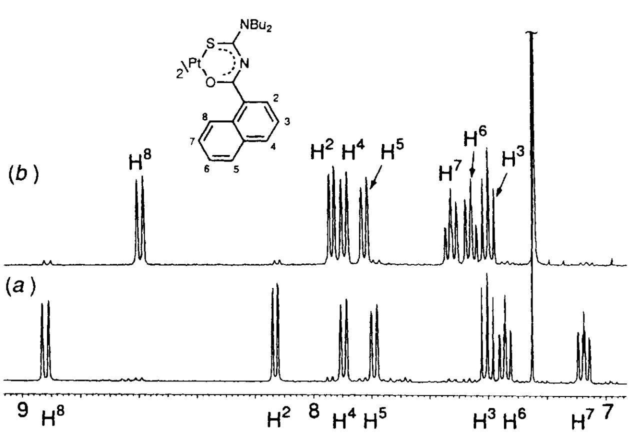

Fig. 2 ^{1}H NMR spectra of the aromatic region for *cis*- (*a*) and *trans*-[PtL$^1{}_2$] (*b*) in CDCl$_3$ (400 MHz, T = 298 K)

C(12). The dihedral angle between planes 1 and 2 is only 29.3(3)° indicating approximate coplanarity of the naphthyl residues and the square plane of the Pt co-ordination sphere.

The ^{1}H NMR spectra of *trans*-[PtL$^1{}_2$] compared to virtually pure *cis*-[PtL$^1{}_2$] (Fig. 2) show some interesting differences, particularly with reference to the chemical shifts of the naphthyl moiety. In *cis*-[PtL$^1{}_2$] the H^8, H^2, H^4 and H^5 resonances are shifted downfield by +0.475, +0.144, +0.013 and +0.045 ppm relative to the uncomplexed ligand HL^1, while H^7, H^6 and H^3 are shielded by −0.408, −0.247 and −0.125 ppm respectively. By contrast for *trans*-[PtL$^1{}_2$], the extent of deshielding for H^8 is reduced substantially to +0.146 ppm while H^2 is shielded by −0.051 ppm relative to the ligand. We ascribe the chemical shift differences (particularly with respect to H^8 and H^2) of these isomers to differing relative orientations of the naphthyl moiety with respect to the square plane of co-ordination. In the case of *trans*-[PtL$^1{}_2$], the crystal structure shows the naphthyl moiety to be approximately coplanar with the square plane of co-ordination. On the other hand, inspection of models of *cis*-[PtL$^1{}_2$] leads to the conclusion that the orientation of the naphthyl moieties must be virtually perpendicular to the co-ordination plane on steric grounds. It is reasonable to postulate that such relative orientations of the naphthyl moiety in *trans*-[PtL$^1{}_2$] and its *cis* isomer persist in solution. Miller *et al.*[14] have shown that ligand protons in planar transition-metal complexes of low symmetry are subject to second-order paramagnetic shielding effects ascribed to the anisotropy in the magnetic susceptibility of the metal ion, so that protons in close proximity to the metal ion above the bonding plane exhibit pronounced downfield shifts. We thus propose that the marked downfield shifts of H^8 and H^2 in *cis*-[PtL$^1{}_2$] may be ascribed to the paramagnetic anisotropy of the Pt^{II} metal ion which these two hydrogen atoms experience as a consequence of the approximately perpendicular orientation of the naphthyl moieties with respect to the plane of co-ordination, in contrast to the case of *trans*-[PtL$^1{}_2$]. The significant shift differences which are observed for H^7 and H^6 for the *cis* isomer (7.092 and 7.363 ppm, respectively) relative to the *trans* (7.546 and 7.476 ppm) may be attributed further to the magnetic anisotropy associated with the ring currents of adjacent naphthyl moieties in the *cis* complex.

The formation of *trans*-[PtL$^1{}_2$] in *ca.* 15% yield alongside the presumably thermodynamically favoured *cis*-[PtL$^1{}_2$] is interesting, and suggests a possible steric effect is operating in the transition state during the formation of these bis(ligand) complexes. We find no evidence for the formation of a corresponding *trans* isomer of *cis*-[PtL$^2{}_2$] despite efforts in this regard.[4] Inspection of the crystal structure of *cis*-[PtL$^2{}_2$] shows the phenyl moieties to be approximately coplanar with the plane of co-ordination, thus ruling out significant transition-state steric interactions between the phenyl rings as postulated for the naphthyl-substituted analogue.

We find no evidence of any thermal isomerization of *cis*-[PtL$^1{}_2$] or *cis*-[PtL$^2{}_2$] analogous to [Pt(L′-*S*,*N*)$_2$] (HL′ = L-methionine) which undergoes facile *cis*–*trans* isomerization in aqueous solution.[15] The *cis*-[PtL$^2{}_2$] complex retains its isomeric integrity on storage above its melting point (170 °C) for 30 min. Further, the possibility of photochemically induced isomerization of *cis*-[PtL$^1{}_2$] in chloroform or chloroform–acetonitrile solution to *trans*-[PtL$^1{}_2$], analogous to the isomerization of *cis*-bis(glycinato)platinum(II),[16] must be excluded since irradiation of authentic *cis*-[PtL$^1{}_2$] in these solvents in quartz cells using a broad-band ultraviolet mercury lamp for 24 h did not result in any isomerization.

Acknowledgements

We thank the University of Cape Town and the Foundation for Research and Development (FRD) for financial assistance and Johnson Matthey for the loan of platinum salts.

References

1 P. Mühl, K. Gloe, F. Dietze, E. Hoyer and L. Beyer, *Z. Chem.*, 1986, **26**, 81.
2 L. Beyer, E. Hoyer, J. Liebscher and H. Hartmann, *Z. Chem.*, 1981, **21**, 81.
3 M. Schuster, *Fresenius' Z. Anal. Chem.*, 1992, **342**, 791.
4 K. R. Koch, A. Irving and M. Matoetoe, *Inorg. Chim. Acta*, 1993, **206**, 193.
5 S. Bourne and K. R. Koch, *J. Chem. Soc., Dalton Trans.*, 1993, 2071.
6 P. Knuuttilla, H. Knuuttilla, H. Hennig and L. Beyer, *Acta Chem. Scand., Ser. A*, 1982, **36**, 541.
7 R. A. Bailey, K. L. Rothaupt and R. K. Kullnig, *Inorg. Chim. Acta*, 1988, **147**, 233.
8 G. Fitzl, L. Beyer, J. Sieler, R. Richter, J. Kaiser and E. Hoyer, *Z. Anorg. Allg. Chem.*, 1977, **433**, 237.
9 I. B. Douglass and F. B. Dains, *J. Am. Chem. Soc.*, 1934, **56**, 719.
10 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
11 G. M. Sheldrick, SHELX 76, A System of Computer Programs for X-Ray Structure Determination, University of Cambridge, 1976.
12 G. M. Sheldrick, SHELXL 93, *J. Appl. Crystallogr.*, in the press.
13 K. R. Koch and C. Sacht, unpublished results.
14 R. G. Miller, R. D. Stauffer, D. R. Fahey and D. R. Panell, *J. Am. Chem. Soc.*, 1970, **92**, 1511.
15 P. S. Murdoch, J. D. Ranford, P. J. Sadler and S. J. Berners-Price, *Inorg. Chem.*, 1993, **32**, 2249.
16 F. Scandola, O. Traverso, V. Balzani, G. L. Zucchini and V. Carassiti, *Inorg. Chim. Acta*, 1967, **1**, 76.

Received 20*th December* 1993; *Communication* 3/07445E