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Intramolecular Hydrogen-bond Controlled Unidentate Co-ordination of Potentially Chelating *N*-Acyl-*N'*-alkylthioureas: Crystal Structure of *cis*-Bis(*N*-benzoyl-*N'*-propylthiourea)dichloroplatinum(II)

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The crystal and molecular structure of *cis*-bis(*N*-benzoyl-*N'*-propylthiourea)dichloroplatinum(II) shows that two *N*-benzoyl-*N'*-propylthiourea molecules co-ordinate to Pt^{II} through the sulfur atom only, the acyl oxygen atom being effectively blocked from co-ordination by an intramolecular hydrogen bond, in contrast to the chelating *N*-benzoyl-*N'*,*N'*-dialkylthiourea analogues.

N-Benzoyl-*N'*-alkyl- and *N*-benzoyl-*N'*,*N'*-dialkyl-thioureas have recently attracted interest in view of their potential use as highly selective reagents for the liquid–liquid extraction,[1,2] preconcentration and separation[3] of the platinum-group metals. The potentially bidentate ligands $RC(O)NHC(S)NR^1R^2$ (HL, R = Ph; R^1, R^2 = alkyl), which may be easily prepared from simple starting materials,[4] form stable neutral complexes with a variety of transition metals.[5] In the case of the divalent d^8 metal ions, only *cis*-$[ML_2]$ complexes have been reported. The crystal structures for M = Ni^{II} and Pd^{II} (R^1, R^2 = Et)[5] and Pt^{II} (R^1, R^2 = Bu),[6] all show very similar co-ordination to the metal in which HL co-ordinates to M^{II} through the sulfur and oxygen atoms, with concomitant loss of a proton, yielding simple square-planar complexes. We have recently shown by means of ^1H and ^{195}Pt NMR spectroscopy that the *cis*-$[PtL_2]$ complexes (L = *N*-benzoyl-*N'*,*N'*-dibutylthioureate anion) may be reversibly protonated in solution to yield cationic *cis*-$[Pt(HL)L]^+$ and *cis*-$[Pt(HL)_2]^{2+}$ species, which may be isolated under certain conditions.[6] By contrast, we find that *N*-benzoyl-*N'*-alkylthioureas (H_2L) show a substantially different co-ordination chemistry: thus we have not been able to isolate a well defined nickel(II) complex with H_2L under any circumstances. Moreover the reported liquid–liquid extraction of platinum-group metals with H_2L differs considerably from the dialkyl analogues. These differences have been ascribed to lower solubilities of the *N'*-monoalkyl substituted ligands, as well as differing electronic effects, in which the +I substituent effect of the alkyl moieties is invoked to lead to enhanced electron densities at the ligand S and O donor atoms.[2]

We have prepared *N*-benzoyl-*N'*-propyl- (H_2L^1) and *N*-benzoyl-*N'*-butyl-thiourea (H_2L^2) and studied their co-ordination to Pt^{II} and Pd^{II}. Treatment of a solution of $[PtCl_4]^{2-}$ with a solution of H_2L^1 under mildly acidic conditions leads to the formation of a complex with stoichiometry $Pt(H_2L^1)_2Cl_2$.‡ The crystal structure of H_2L^2 (ref. 7) shows the molecule to be locked into a planar six-membered O–C–N–C–N–H ring by means of an intramolecular N–H ··· O hydrogen bond. A very similar structure for H_2L^1 has recently been reported.[8] These structures suggest the possibility of intramolecular hydrogen-bond controlled co-ordination of these potentially bidentate ligands.

We here report the crystal structure§ of *cis*-bis(*N*-benzoyl-*N'*-propylthiourea)dichloroplatinum(II) **1**, as depicted in Fig. 1. From the structure it is evident that the two ligand molecules bind to Pt^{II} *via* the sulfur atoms only, the carbonyl oxygen atom being locked into a ring by a N–H ··· O hydrogen bond similar to that in the free ligands H_2L^1 and H_2L^2. In **1** the

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‡ To a stirred, warm (60 °C), solution (30 cm^3, dioxane–1 mol dm^{-3} HCl, 2:1 v/v) of H_2L^1 (112 mg, 0.5 mmol), was added dropwise a solution of $K_2[PtCl_4]$ (103.8 mg, 0.25 mmol) in the same solvent (30 cm^3) over 10–15 min. The solution was allowed to stir for a further 30 min at 60 °C. On cooling the mixture in ice, after the addition of cold water (200 cm^3), a bright yellow precipitate was obtained which was collected by filtration. Recrystallization from chloroform–ethanol and drying in vacuum gave *cis*-$[Pt(H_2L^1)_2Cl_2]$ **1** in 82% yield, m.p. 133–135 °C (Found: C, 37.3; H, 3.5; N, 7.8. $C_{22}H_{28}Cl_2N_4O_2PtS_2$ requires C, 37.20; H, 3.95; N, 7.8%).

§ Crystal data: $C_{22}H_{28}Cl_2N_4O_2PtS_2$, yellow crystals 0.13 × 0.13 × 0.16 mm, *M* = 710.616, space group $P2_1/n$, a = 11.006(2), b = 8.363(2), c = 28.650(6) Å, β = 92.83(2)°, U = 2633.82(97) $Å^3$, Z = 4, D_c = 1.792 g cm^{-3}, $F(000)$ = 1392, μ(Mo-Kα) = 57.653 cm^{-1}. 5060 Reflections were collected on a four-circle diffractometer with $2\theta_{max}$ = 50°. 2682 Reflections with $I \geqslant 2\sigma(I)$ were used for the structure determination and refinement. The structure was solved using the automatic Patterson function of SHELXS 86[9] and refined using SHELX 76,[10] including anisotropic refinement of all non-hydrogen atoms. Hydrogen atoms involved in hydrogen bonding [H(10A) and H(10B)] were located and refined independently. All other H atoms were placed geometrically and refined with a common isotropic thermal parameter. The weighting scheme $w = [\sigma^2(F) + 0.002F^2]^{-1}$ gave satisfactory results, yielding at final convergence R = 0.077, R' = 0.0802 and S = 2.6469 for 313 refined parameters, with maximum and minimum residual electron densities of 4.6 and −2.1 e $Å^{-3}$ in the region of the Pt atom. Atomic co-ordinates, 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.*, 1993, Issue 1, pp. xxiii–xxviii.

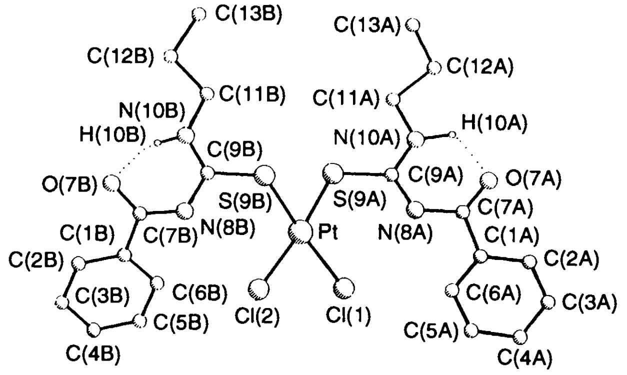

Fig. 1 The molecular structure of *cis*-bis(*N*-benzoyl-*N*′-propylthiourea)dichloroplatinum(II) **1** showing the numbering scheme adopted (see text for significant bond lengths and angles)

O–C–N–C–N–H ring of the ligands A and B is also nearly planar, with maximum deviations of 0.11 and 0.24 Å respectively. The thioamide H atoms involved in the hydrogen bond were located by means of a Fourier difference map and refined independently with the N–H bond length constrained to 1.00(2) Å. The structure of the co-ordinated ligands is remarkably similar to that of the free ligand, the corresponding bond lengths involved in the O–C–N–C–N–H ring of the former being comparable to the free ligand:[8] C(9A)–S(9A) 1.699(23), C(9B)–S(9B) 1.696(21), C(9A)–N(8A) 1.366(26), C(9A)–N(10A) 1.307(28), C(9B)–N(10B) 1.273(25), C(7A)–O(7A) 1.223(25) and C(7B)–O(7B) 1.259(23) Å. The mean Pt–S bond length of 2.278(6) Å is slightly shorter than the typical range of 2.309–2.335 Å observed for tetrakis(thiourea)platinum(II) cations,[11,12] but somewhat longer than in the related complex *cis*-bis(*N*-benzoyl-*N*′,*N*′-dibutylthiourea)platinum(II) [mean Pt–S 2.232(2), Pt–O 2.022(5) Å].[6] The interatomic distances in **1**, between N(8A) ··· Cl(1) and N(8B) ··· Cl(2) at 3.2 Å are considerably shorter than the sum of the covalent radii of Cl and N at 3.4 Å,[13] suggesting two N–H ··· Cl hydrogen bonds, although the H atoms presumed to be involved in these interactions could not be located crystallographically. Nevertheless such interactions may account for the marked distortion of the co-ordination sphere of Pt^{II} from ideal square-planar geometry, since the bond angles S(9A)–Pt–Cl(2) and S(9B)–Pt–Cl(1) at 172.6 and 174.4° respectively are significantly less than 180°, while S(9A)–Pt–Cl(1) (94.1°), S(9B)–Pt–Cl(2) (93.2°) and S(9B)–Pt–S(9A) (88.9°) deviate from 90°. There do not appear to be any other significant intermolecular contacts.

Apart from the interesting unidentate co-ordination of H_2L^1, it is noteworthy that suitable crystals of **1** were obtained from a sample of analytically pure $[Pt(H_2L^1)_2Cl_2]$, which was found to consist of a 2.3:1 mixture of the *cis* and *trans* isomers. The ^1H NMR spectrum of this mixture shows two sharp N–H resonances at δ 11.77 and 11.53 assigned to the amide protons, and two broad, partly resolved triplets ($^3J \approx 13$ Hz) at δ 11.12 and 11.09 assigned to the N–H ··· O hydrogen-bonded thioamide protons, all in a 2.3:1 relative ratio, respectively. The ^{195}Pt NMR spectrum [30 °C, $CDCl_3$, relative to external H_2PtCl_6, $\delta(^{195}Pt)$ 0][14] shows only two resonances at δ −3219 and −3040 in the same relative ratio, assigned to the *cis* and *trans* isomers respectively. This argument is based on the generally observed trend that the ^{195}Pt chemical shifts for *cis*-$[PtL_2Cl_2]$ complexes are upfield relative to the corresponding *trans* isomer.[14] In view of the high *trans* effect of unidentate thioureas,[15] the fact that **1** is the *cis* isomer, which also appears to predominate in solution, is unexpectedly interesting. In this context, the recent observation by Sadler and co-workers[16] concerning the reactions of L-methionine (HL) with $[PtCl_4]^{2-}$ deserves comment; at low pH (*ca.* 2) the predominant complex in solution, arising from a 2:1 HL:$[PtCl_4]^{2-}$ reaction, was found to be the partially ring-opened *cis*-[Pt(HL-*S*,*N*)(H_2L-*S*)Cl]$^{2+}$ species, which converts reversibly into predominantly the ring-closed *cis*-[Pt(L-*S*,*N*)$_2$] complex at neutral pH, with only minor amounts of the corresponding *trans* isomer being present. Nevertheless in the present work, the very similar ^1H NMR spectra of platinum(II) complexes with analogous *N*-benzoyl-*N*′-isopropyl- and *N*-benzoyl-*N*′-phenyl-thiourea, suggests that the described intramolecular hydrogen-bond controlled unidentate co-ordination of these types of ligands may be a general phenomenon, accounting for the substantial differences in co-ordination behaviour between the *N*-acyl-*N*′-monoalkyl- and *N*-acyl-*N*′,*N*′-dialkyl-thioureas. Further work aimed at understanding and exploiting these differences for the possible control of selectivity of these ligands towards the platinum-group metals is underway.

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References

1 K.-H. König, M. Schuster, G. Schneeweis and B. Steinbrech, *Fresenius' Z. Anal. Chem.*, 1984, **325**, 621.
2 P. Vest, M. Schuster and K.-H. König, *Fresenius' Z. Anal. Chem.*, 1989, **335**, 759.
3 M. Schuster, *Fresenius' Z. Anal. Chem.*, 1992, **342**, 791.
4 I. B. Douglass and F. B. Dains, *J. Am. Chem. Soc.*, 1934, **56**, 719.
5 L. Beyer and E. Hoyer, *Z. Chem.*, 1981, **21**, 81.
6 K. R. Koch, A. Irving and M. Matoetoe, *Inorg. Chim. Acta*, 1993, **206**, 193.
7 S. Bourne, T. Grimmbacher and K. R. Koch, unpublished work.
8 A. Drago, Yu Shepelev, F. Fajardo, F. Alvarez and R. Pomes, *Acta Crystallogr., Sect. C*, 1989, **45**, 1192.
9 G. M. Sheldrick, SHELXS 86, in *Crystallographic Computing 3*, eds. G. M. Sheldrick, C. Kruger and R. Goddard. Oxford University Press, 1985, p. 175.
10 G. M. Sheldrick, SHELX 76, University of Cambridge, 1976.
11 R. L. Girling, K. K. Chatterjee and E. L. Amma, *Inorg. Chim. Acta*, 1973, **7**, 557.
12 F. Bachechi, L. Zambonelli and G. Marcotrigiano, *Inorg. Chim. Acta*, 1976, **17**, 225.
13 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1984, p. 64.
14 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247.
15 F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 1967, p. 355.
16 R. E. Norman, J. D. Ranford and P. J. Sadler, *Inorg. Chem.*, 1992, **31**, 877.

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