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# Competitive bulk liquid membrane transport and solvent extraction of some transition and post-transition metal ions using acylthiourea ligands as ionophores

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Competitive transport experiments involving metal ions from an aqueous source phase through a chloroform membrane into an aqueous receiving phase have been carried out using a series of acylthiourea ligands as the ionophore present in the organic phase. The source phase contained equimolar concentrations of cobalt(II), nickel(II), copper(II), zinc(II), silver(I), cadmium(II) and lead(II) with the source and receiving phases being buffered at a number of different pHs. Transport selectivity was observed for silver(I) in all but one case. Selectivity for silver(I) was also observed in a series of parallel solvent extraction experiments carried out under similar source and membrane phase conditions. An X-ray diffraction study of the silver(I) complex of the *N,N*-dibutyl-*N*′-benzoylthiourea from this series is reported. There are two crystallographically independent molecules in the asymmetric unit and each molecule consists of four silver(I) ligand complex units, hence giving rise to $Z = 8$. In each molecule, both chelate and monodentate co-ordination modes of complexation to silver(I) are evident. Hence, each silver is co-ordinated to a sulfur and oxygen atom from one ligand and to a shared (bridging) sulfur from another ligand. Each silver atom is thus co-ordinated to three donor atoms.

## Introduction

We recently published a preliminary report illustrating the highly selective Ag(I) bulk liquid membrane transport using *N,N*-diethyl-*N*′-camphanylthiourea as well as the unusual crystal structure formed by this complex.[1] The *N,N*-dialkyl-*N*′-aroylthioureas have long been known since their first synthesis by Neucki in 1873.[2] The co-ordination chemistry and potential applications (solvent extraction) of mainly *N,N*-dialkyl-*N*′-aroylthioureas with transition metals was first explored by the groups of Hoyer and Beyer[3] and later König, Schuster *et al.*[4] explored the similar chemistry of these ligands with the platinum group metals. We have exploited these ligands for the analytical and process chemistry of mainly the platinum group metals.[5,6] The favourable physicochemical properties of selected *N,N*-dialkyl-*N*′-acylthioureas have resulted in the convenient HPLC determination of platinum group metals.[7]

There have been many reports of the transport of transition and post-transition metal ions through bulk liquid membranes using synthetic ionophores. These included the use of mixed-donor acyclic ligands,[8] oxygen–nitrogen donor macrocycles[9] and thioether donor macrocycles.[10] The objective of these studies has been to obtain better reagents for the separation of metal ions in mining, medical and a number of analytical applications. A number of studies have looked at the factors which influence the transport efficiency[11–13] and one study has shown that the transport-limiting step differs from one system to the next.[14]

To date, there have not been studies using acylthiourea ligands for potential metal ion transport. We report herein the first comprehensive study of the use of these ligands for metal ion transport using bulk liquid membranes, with particular reference to the results which were obtained with the ligand *N,N*-diethyl-*N*′-camphanylthiourea.[1] This ligand showed remarkably high and selective transport rates for Ag(I) in the presence of several other transition metal ions. We also carried out comparative competitive liquid–liquid extraction experiments using the above ligands with the seven metal ions. The crystal structure of the silver(I) complex with $HL^1$ is also described.

In this study we used the three phase arrangement and the same cell design as that of Lindoy *et al.*,[15] which involves two buffered aqueous phases (source and receiving phases) separated by an immiscible organic phase (chloroform) incorporating the ionophore. We have buffered the source and receiving phases at a number of pHs to examine the effect which this has on the transport of metal ions.

## Experimental

### Materials

All reagents were of analytical grade and used without further purification. All ligands were synthesised according to the method of Douglass and Dains[16] and characterised by means

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of elemental analysis, IR and NMR, as described previously.[5,17] All aqueous solutions were prepared using deionised water. Chloroform used for the membrane phase was presaturated with water by shaking a two phase water–chloroform mixture, then removing the aqueous phase.

### Preparation and crystallization of $[Ag(L^1)]_4$

The ligand *N,N*-dibutyl-*N′*-benzoylthiourea, $HL^1$ (0.10 g, 0.34 mmol) was dissolved in a 30 ml solvent mixture of acetonitrile–water in a volume ratio of 5 : 1, respectively. Sodium acetate (0.09 g, 0.684 mmol), dissolved in a minimum volume of water, was added to the ligand solution and the resulting reaction mixture was warmed under reflux in an oil bath at 50 °C for 45 min. To this solution was added a solution of silver nitrate (0.06 g, 0.34 mmol), dissolved in a minimum volume of water, drop-wise, after which the mixture was heated to reflux at 60 °C for 1 h. At this stage, the colour of the reaction mixture was milky which became clear on addition of additional acetonitrile.

The reaction mixture was cooled to room temperature, after which excess water (about 20 ml) was added to the flask, to precipitate the complex and to dissolve the remaining sodium acetate. The white precipitate which was obtained after overnight storage in a refrigerator was collected by filtration and recrystallised from an acetonitrile–chloroform (1 : 1) mixture. Colourless crystals were obtained after 4 days of slow evaporation of the solvent mixture at room temperature. The crystals were characterised by melting point determination, elemental (C, H, N and S) analysis and X-ray structure determination. Mp: 113–114 °C. (Found: C, 48.44; H, 5.83; N, 7.03; S, 7.73%; $C_{16}H_{23}N_2SOAg$ required C, 48.13; H, 5.81; N, 7.02; S, 8.03%.)

### Membrane transport and solvent extraction

An aqueous source phase containing an equimolar mixture of the seven metal ions cobalt(II), copper(II), lead(II), silver(I), cadmium(II), zinc(II) and nickel(II), (10 $cm^3$) and an aqueous receiving phase (30 $cm^3$) were separated by a water presaturated chloroform membrane phase containing the ligand (50 $cm^3$) and $4 \times 10^{-3}$ mol $dm^{-3}$ palmitic acid. The concentration of the metal ions was $1 \times 10^{-2}$ mol $dm^{-3}$ and that of the chosen ligand was $1 \times 10^{-3}$ mol $dm^{-3}$ or $2 \times 10^{-3}$ mol $dm^{-3}$ in separate experiments. The cell details are the same as those used by Lindoy *et al.*[15]

The membrane phase, the source phase and the receiving phase were then gently transferred in this respective order into the cells. The cells were thermostated at 25 °C and stirred at 10 rpm by means of a coupled single geared synchronous motor. Under these conditions, not only was the stirring process consistent, but also the interfaces between the organic membrane and the two aqueous phases remained flat and well defined and transport allowed to take place, against a back gradient of protons. The cells were covered with cover slips in order to prevent evaporation of solvents over the 24 h period and then entirely covered by aluminium foil in order to prevent the light-induced reduction of Ag(I) in the source phase. All transport experiments were terminated after 24 h and the amount of metal ion transported from the source phase to the receiving phase over this period was determined by atomic absorption spectroscopy (AAS) and confirmed by inductively coupled plasma-optical emission spectroscopy (ICP-OES). The experimental results obtained from both techniques did not differ by more than 4%.

Small samples for analysis were taken from both the source and receiving phases of each duplicate run after each experiment and analysed. The average flux rate, $J$ (mol per 24 h), for each transport experiment was calculated based on the quantity of metal ions transported into the receiving phase in a 24 h period. The transport results are quoted as the average values obtained from the duplicate runs carried out in parallel; in all cases the flux values obtained did not differ by more than 5%. $J$ values equal to or less than $2.2 \times 10^{-8}$ mol per 24 h were assumed to be within experimental error of zero and have been ignored in the analysis of results.

For the 'competitive' metal ion extraction experiments, the reagents used were identical to those employed in the transport experiments. The aqueous phase was buffered at pH = 5.0 with sodium acetate–acetic acid buffer and contained equal concentrations ($1 \times 10^{-2}$ mol $dm^{-3}$) of cobalt(II), copper(II), lead(II), silver(I), cadmium(II), zinc(II) and nickel(II) as their respective nitrate salts. The chloroform membrane contained the ligands at concentrations of $1 \times 10^{-3}$ mol $dm^{-3}$ and $2 \times 10^{-3}$ mol $dm^{-3}$ in separate experiments and (as was done in the transport experiments), $4 \times 10^{-3}$ mol $dm^{-3}$ palmitic acid. The aqueous source phase (3 ml) and the chloroform membrane (15 ml) were contained in a tightly capped polytop vial, wrapped with parafilm and aluminium foil to prevent light-induced reduction of Ag(I). These vials were shaken at 120 cycles per minute for 24 h on a Labcon oscillating shaker at 25 °C. The determination of metal ions was performed by AAS and confirmed by ICP-OES. The results are quoted as the average value obtained from duplicate runs. Any apparent extraction of a metal ion of less than 2% relative, was assumed to be within the experimental error of zero and hence ignored in the treatment of the results. In all cases, the values between any two duplicate runs did not differ by more than 2%.

### Crystallographic data collection and structure determination

A suitable crystal was mounted on a thin glass fibre and coated in silicone-based oil to prevent decomposition. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å) with a detector to crystal distance of 45 mm. 663 oscillation frames were recorded, each of width 1° in diameter, followed by 422 frames of 1° width in $\omega$ (with $\kappa \neq 0$). Crystals were indexed from the first ten frames using the DENZO package[18] and positional data were refined along with diffractometer constants to give the final cell parameters. Integration and scaling (DENZO, Scalepack[18]) resulted in unique data sets corrected for Lorentz-polarisation effects and for the effects of crystal decay and absorption by a combination of averaging of equivalent reflections and an overall volume and scaling correction. Crystallographic data are recorded in Table 1. The structure was solved using SHELXS-97[19] and developed *via* alternating least squares cycles and Fourier difference synthesis (SHELXL-97[19]) with the aid of the interface

**Table 1** The crystallographic data and structure refinement for tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) silver(I)] complex

| | |
|---|---|
| Empirical formula | $C_{64}H_{92}Ag_4N_8O_4S_4$ |
| Formula weight | 1597.216 |
| $T$/K | 193(2) |
| $\lambda$/Å | 0.710 73 |
| Crystal system and space group | Monoclinic, $P2_1/n$ |
| Unit cell dimensions | $a$ = 17.805(4) Å $\alpha$ = 90°<br>$b$ = 21.759(4) Å $\beta$ = 96.34(3)°<br>$c$ = 36.438(7) Å $\gamma$ = 90°. |
| $V$/Å$^3$ | 14 030(5) |
| $Z$, Calculated density | 8, 1.516 g cm$^{-3}$ |
| Absorption coefficient. ($\mu$/mm$^{-1}$) | 1.269 |
| $F$(000) | 6560 |
| Crystal size | 0.12 × 0.20 × 0.25 mm |
| $\Theta$ range for data collection | 2.85 to 25.00° |
| Limiting indices | $-21 \le h \le 21$, $-25 \le k \le 25$,<br>$-43 \le l \le 43$ |
| Completeness to $\theta$ = 27.87 | 94.2% |
| Max. and min. transmission | 0.8626 and 0.7421 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data, restraints, parameters | 23 275, 0, 1334 |
| Goodness-of-fit on $F^2$ | 1.030 |
| Reflections collected, unique | 41 998, 23 275 [$R$(int) = 0.0265] |
| Final $R$ indices [$I > 2\sigma(I)$] | 0.0537, 0.0918 |
| $R$ indices (all data) | $R1$ = 0.1441, w$R2$ = 0.1692 |
| Largest diff. peak and hole | 0.709 and −0.537 e A$^{-3}$ |

program X-SEED.[20] There are two crystallographically independent molecules in the asymmetric unit, giving rise to $Z = 8$ in $P2_1/n$.† All non-hydrogen atoms were modelled anisotropically, except for the carbon atoms in the butyl chains. Since the carbon atoms in the butyl chains have very high thermal motion, they were modelled with isotropic displacement parameters, and over two disordered positions in some cases (site occupancy factors were independently modelled for each disordered chain). Hydrogen atoms on the phenyl rings were assigned an isotropic thermal parameter of 1.2 times that of their parent atom and refined using a riding model. No hydrogens were placed on the butyl chains. The different views and sections of the crystal structure are shown in Fig. 2 and 3.

## Results and discussion

In this section, ligands having similar structures are grouped together for the purpose of the discussion. Structures of ligands are shown in Fig. 1 and all transport results are shown in Table 2.

Ligands $HL^1$, $HL^2$ and $HL^3$ all posses a benzoyl group and an acylthiourea motif in their structures but differ in their substituent groups.

For $HL^1$ and $HL^2$, a source phase pH of 5.5 and a receiving phase pH of 1.0 were adopted as optimum conditions, so that the effect of varying the ligand concentration from $1 \times 10^{-3}$ to $2 \times 10^{-3}$ mol dm$^{-3}$ on the transport efficiency and selectivity for Ag(I) could be studied. For $HL^3$, we have studied the effect of varying the ligand concentration as well as pH of the source phase.

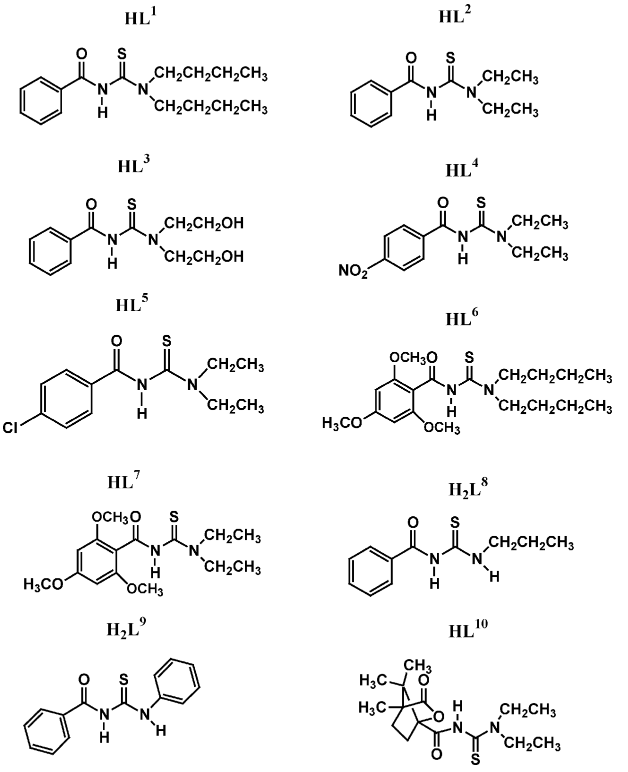

**Fig. 1** Acylthiourea ligands investigated as potential ionophores.

Under the experimental conditions employed, $HL^1$ and $HL^2$ are selective for Ag(I) whereas $HL^3$ selectively transports Cu(II). It can be seen from Table 2 that the percentage transport of Ag(I) by $HL^1$ is higher than that of $HL^2$. The sum ($^{Ag}T_r\%$ + $^{Ag}T_M\%$) [see Table 2 for key and abbreviations], which is a measure of the interaction between the ligands and Ag(I), is slightly higher for $HL^1$ than $HL^2$. $HL^1$ is more soluble in chloroform compared to $HL^2$, so the higher percentage transport of Ag(I) by $HL^1$ can be the result of an increased lipophilicity of the ligand because of its longer alkyl substituents (butyl groups) compared to those of $HL^2$ where the substituents are ethyl groups. That $HL^3$ is selective for Cu(II) compared with Ag(I) can be attributed to the presence of the two –OH groups attached to the alkyl end of the ligand. It

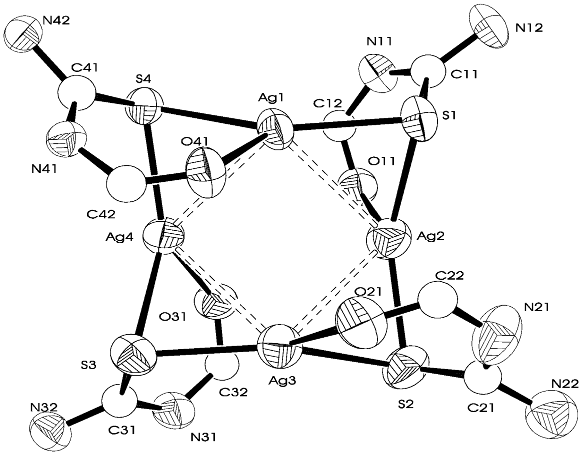

**Fig. 2** Partial structure and numbering scheme for $[Ag(L^1)]_4$ complex. Phenyl and butyl groups are omitted for clarity.

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† CCDC reference number 609098. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b603802f

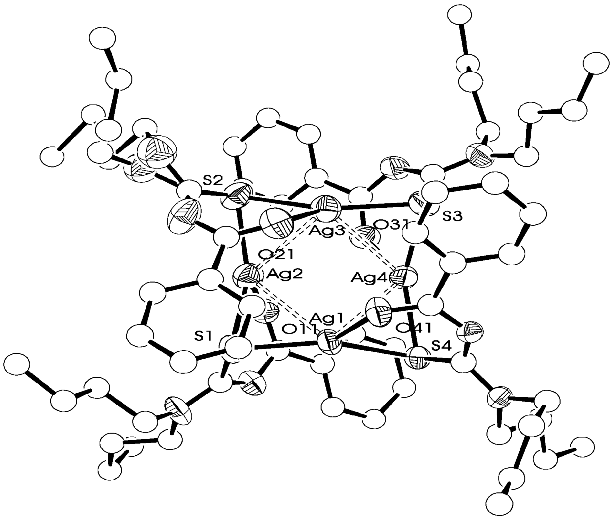

**Fig. 3** The structure of $[Ag(L^1)]_4$ complex showing one of the two molecules in the asymmetric unit.

is interesting and it shows that apparently small changes in ligand structure have a significant effect on relative selectivity. For $HL^3$, the sum ($^{Ag}T_r\%$ + $^{Ag}T_M\%$) is greater than ($^{Cu}T_r\%$ + $^{Cu}T_M\%$). Only Cu(II) is transported into the receiving phase by ligand $HL^3$. This suggests that although about 95% of Ag(I) is extracted from the source phase into the membrane phase, it is not stripped into the receiving phase at pH = 1.0 (see Table 2). On the other hand, although Cu(II) was not transported into the membrane phase as efficiently as Ag(I), about 13% of the total Cu(II) originally present in the source phase was transported into the receiving phase. Therefore, it appears that the formation constant of $HL^3$ must be substantially higher for Ag(I) than Cu(II), not allowing the release of Ag(I) from the membrane phase into the receiving phase. Hence, $HL^3$ is a better transport ionophore for Cu(II) compared to Ag(I).

As can be seen from the table, the sum ($^{Cu}T_M\%$ + $^{Ag}T_M\%$) exceeds 100%. This indicates that the ligand $HL^3$ must be simultaneously coordinating with both Ag(I) and Cu(II) ions, thus transporting Cu(II) into the receiving phase while simultaneously extracting Ag(I) into the membrane phase. Therefore, we speculate that the ligand may be binding to Ag(I) ion through the sulfur and oxygen donor atoms of the acylthiourea moiety, and perhaps to Cu(II) through the oxygen atoms of the two –OH groups.

Attaching electron-withdrawing groups to the benzoyl moiety and examining these effects on metal ion transport, is reported for ligands $HL^4$ and $HL^5$. Experiments were carried out with these two ligands, where the pH of the aqueous phases and ligand concentration were varied. Unfortunately, these ligands, however, differ greatly in their solubility in chloroform. Ligand $HL^5$ is very soluble, whereas ligand $HL^4$ is only slightly soluble. Nevertheless, both ligands are selective for Ag(I), with only a small percentage of Cu(II) also being transported. Results indicate that ligand $HL^5$ has a higher efficiency and better selectivity for Ag(I).

At a ligand concentration of $2 \times 10^{-3}$ mol dm$^{-3}$, the optimum pH values of the source and receiving phase, which resulted in selective and efficient transport of Ag(I) by $HL^5$, were found to be 5.5 and 1.0, respectively. Decreasing the pH of the source phase from 5.5 to 5.0 did not bring about a significant change in Ag(I) transport.

When comparing ligand $HL^2$ with ligands $HL^4$ and $HL^5$, since they all have diethyl chains on nitrogen, ligand $HL^5$ shows the highest transport of Ag(I) and the values for ligands $HL^2$ and $HL^4$ are comparable.

The effect of attaching electron-releasing substituents to *N*,*N*-dialkyl-*N*′-benzoylthioureas on transport efficiency and selectivity was studied using ligands $HL^6$ and $HL^7$. As can be seen from their structures, both ligands possess methoxy substituents at positions $C_2$, $C_4$ and $C_6$. $HL^6$ and $HL^7$ are both soluble in chloroform which makes these ligands suitable candidates for transport studies.

The effect of varying the pH of the source phase from 5.0 to 5.5 and 6.0 was studied for these two ligands which resulted in no significant change in the percentage transport of Ag(I) by either ligand. Under the experimental conditions employed,

**Table 2** *J* values for the competitive metal ion transport studies involving $HL^1$–$HL^{10}$. The experimental conditions were: pH of the source phase = 5.5, pH of receiving phase = 1.0 and concentration of ligand = 0.002 mol dm$^{-3}$

| | Metal ion transport, $J$/mol h$^{-1}$ × $10^{-7}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Ligand number | $HL^1$ | $HL^2$ | $HL^3$ | $HL^4$ | $HL^5$ | $HL^6$ | $HL^7$ | $H_2L^8$ | $H_2L^9$ | $HL^{10}$ [a] |
| Co(II) | — | — | — | — | — | — | — | — | — | — |
| Ni(II) | — | — | — | — | — | — | — | — | — | — |
| Cu(II) | 2.2 | — | 5.4 | 1.0 | 1.8 | 2.7 | 1.7 | — | — | — |
| Zn(II) | — | — | — | — | — | — | — | — | — | — |
| Ag(I) | 18 | 11 | — | 9.8 | 20 | 13 | 12 | 0.6 | — | 34 |
| Cd(II) | — | — | — | — | — | — | — | — | — | — |
| Pb(II)[b] | — | — | — | — | — | — | — | — | — | — |
| $^{Ag}T_r\%$ | 42 | 26 | — | 23 | 48 | 31 | 29 | 1.5 | — | 81 |
| $^{Ag}T_M\%$ | 43 | 57 | 95 | 41 | 36 | 38 | 35 | 95 | 57 | 12 |
| $^{Cu}T_r\%$ | 5.4 | — | 13 | 2.4 | 4.4 | 6.6 | 4.2 | — | — | 12 |
| $^{Cu}T_M\%$ | — | 2.5 | 16 | 4.2 | — | 5.8 | 2.3 | — | 5.0 | 7.2 |
| $\eta$(Ag(I)/Cu(II))[c] | 7.8 | $\eta \rightarrow \infty$ | $\eta = 0$ | 9.6 | 11 | 4.7 | 6.9 | $\eta \rightarrow \infty$ | None | 6.8 |

[a] Ligand $HL^{10}$ results from ref. 1 for comparison. [b] $^{Ag}T_r\%$ = Percentage of Ag(I) transported into the receiving phase. $^{Ag}T_M\%$ = Percentage of Ag(I) transported into the membrane phase. $^{Cu}T_r\%$ = Percentage of Cu(II) transported into the receiving phase. $^{Cu}T_M\%$ = Percentage of Cu(II) transported into the membrane phase. [c] $\eta(\mathrm{Ag(I)/Cu(II)}) = \frac{^{Ag}T_r\%}{^{Cu}T_r\%}$

both $HL^6$ and $HL^7$ showed clear selectivity for Ag(I), with ligand $HL^6$ being only slightly more efficient than ligand $HL^7$. However, as can be seen from Table 2, the selectivity factor for Ag(I) compared to Cu(II) is higher for ligand $HL^7$ than ligand $HL^6$. Comparison of ligand $HL^6$ with $HL^1$ shows that ligand $HL^1$ transports Ag(I) better than ligand $HL^6$ (both have dibutyl chains). Ag(I) transport by $HL^7$ results are comparable to those of ligand $HL^2$ (where both have diethyl chains).

The effect of varying the concentration of $HL^6$ and $HL^7$ on transport efficiency and selectivity was also studied. The selectivity factor, $\eta$(Ag(I)/Cu(II)), decreases with an increase in the concentration of the ligands from $1 \times 10^{-3}$ to $2 \times 10^{-3}$ mol $dm^{-3}$. A further increase in ligand $HL^6$ concentration from $2 \times 10^{-3}$ mol $dm^{-3}$ to $4 \times 10^{-3}$ mol $dm^{-3}$ also resulted in a drastic decrease in $\eta$(Ag(I)/Cu(II)). From the results obtained, it is evident that the transport of Ag(I) by ligands $HL^6$ and $HL^7$ is optimum when the ligand concentration is $2 \times 10^{-3}$ mol $dm^{-3}$ and the pH value of the source phase and receiving phase are set at 5.5 and 1.0, respectively.

Ligands $H_2L^8$ and $H_2L^9$ are both soluble in chloroform. These are both mono-alkyl substituted ligands and are grouped together and it was found that under the experimental conditions employed, these ligands are not good at transporting any of the seven metal ions. This also mirrors their poor performance in the solvent extraction of the platinum group metals.[4]

Under the experimental conditions reported in Table 2, 95% of the Ag(I) ion initially present in the source phase was extracted into the membrane phase using $H_2L^8$ but only about 1.5% of Ag(I) was stripped into the receiving phase. This indicates that the formation constant of Ag(I) with $H_2L^8$ is probably too high which thus inhibits the release of the complexed Ag(I) from the membrane phase into the receiving phase. Therefore, this ligand can be a good extracting reagent but not a good transport ionophore for Ag(I). Ligand $H_2L^9$ did not transport any of the seven metal ions in the source phase, but there is a substantial quantity of Ag(I) in the membrane, this being once again most likely due to a large formation constant with Ag(I).

Throughout the transport experiments, we have incorporated $4 \times 10^{-3}$ mol $dm^{-3}$ palmitic acid in the membrane phase and shown that at this concentration it does not transport any of the metal ions in the source phase. Palmitic acid is widely used in transport experiments involving a variety of ligands as ionophores.[9,21] Since the metal ions that we studied are in the form of nitrate salts, $NO_3^-$ may be transported as counter ions along with the divalent metal ions into the receiving phase in order to maintain electro-neutrality through ion pairing or adduct formation. Therefore, to avoid the uptake of nitrate ions, it becomes important to incorporate palmitic acid into the chloroform membrane. An additional benefit of adding lipophilicity in the form of the long-chain acid is to inhibit any "bleeding" of "partially" hydrophilic species (such as the protonated or deprotonated ionophore and/or its corresponding charged metal complex) from the organic membrane phase into either of the aqueous phases.[21–23]

The fact that there is a large amount of metal ion in the receiving phase compared to the amount of ionophore used and because we have used the pH gradient method, it is most likely that the ionophore is transporting the metal ion as a deprotonated species and then becomes protonated again at the membrane phase–receiving phase interface.

### Competitive metal ion liquid–liquid extraction studies

In order to understand the membrane transport results better, a comparative study of liquid–liquid extraction of Ag(I) from a mixture of the metal ions: Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) with the above ligands was conducted.

All results are summarized in Fig. 4. Ligands are grouped in exactly the same way as they were for the discussion of the transport studies.

Under the conditions employed, consistent to the transport results, $HL^1$ and $HL^2$ showed selective extraction for Ag(I) compared with the other six metal ions. At a concentration of $2 \times 10^{-3}$ mol $dm^{-3}$, ligand $HL^1$ extracted about 91% of Ag(I) and 4.5% of Cu(II). When the ligand concentration was decreased by half, the percentage extraction of Ag(I) by ligand $HL^1$ was decreased as expected (only about 52% Ag(I) was extracted). Although the decrease in the concentration of ligand $HL^1$ from $2 \times 10^{-3}$ mol $dm^{-3}$ to $1 \times 10^{-3}$ mol $dm^{-3}$ resulted in a decrease in the overall extraction efficiency for Ag(I), the selectivity for Ag(I) over Cu(II) was enhanced. A similar trend and percentage of Ag(I) extraction was observed with ligand $HL^2$.

The crystal structure data of ligand $HL^1$ and ligand $HL^2$ with Ag(I) shows a 1 : 1 mole ratio stoichiometry.[32] Therefore, if it is assumed that this structure mirrors conditions in solution, $2 \times 10^{-3}$ mol $dm^{-3}$ ($3 \times 10^{-5}$ mol) of the ligands ($HL^1$ or $HL^2$) is theoretically required to extract the total amount of Ag(I) ($1 \times 10^{-2}$ mol $dm^{-3}$, $3 \times 10^{-5}$ mol) completely in the aqueous phase.

In the case of $HL^3$, Ag(I) and Cu(II) were co-extracted by 92% and 41%, respectively; extraction results are consistent with the transport results obtained, which showed that $HL^3$ transported relatively more Ag(I) than Cu(II) into the membrane phase (see Table 2). A decrease in the concentration of $HL^3$ from $2 \times 10^{-3}$ mol $dm^{-3}$ to $1 \times 10^{-3}$ mol $dm^{-3}$ did not

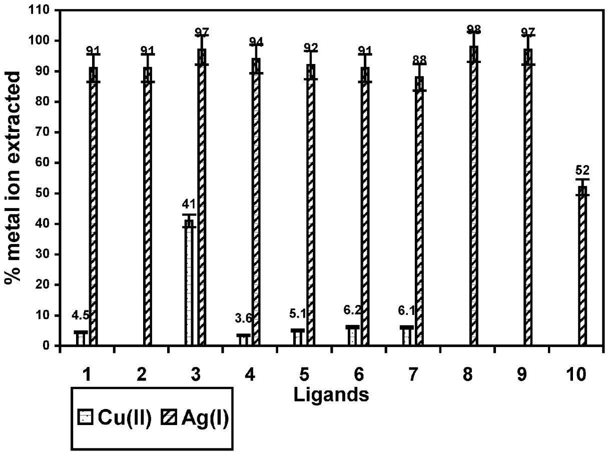

**Fig. 4** Comparison of the competitive extraction studies involving all ligands. The experimental conditions were: pH of the aqueous phase = 5.0 and concentration of ligand = $2 \times 10^{-3}$ mol $dm^{-3}$. 1 represents $HL^1$; 2 represents $HL^2$, *etc.*

significantly affect the percentage extraction of Ag(I) but decreased the percentage extraction of Cu(II) from 41% to 31%. In order to understand this result, further studies of ligand $HL^3$ with Ag(I) and Cu(II) in solution are required.

At a ligand concentration of $2 \times 10^{-3}$ mol $dm^{-3}$, the extraction efficiency and selectivity of ligands $HL^1$–$HL^3$ for Ag(I) follows the order: $HL^3 > HL^2 \cong HL^1$ for efficiency and $HL^2 > HL^1 > HL^3$ for selectivity. Therefore, based on the above results, we can say that varying the alkyl end of a benzoylthiourea ligand from butyl to ethyl enhances selectivity for Ag(I) extraction. However, introducing more oxygen donor atoms by adding hydroxyl-groups to the alkyl end of $HL^2$ to give $HL^3$, resulted in the extraction of Cu(II) together with Ag(I).

At a ligand concentration of $2 \times 10^{-3}$ mol $dm^{-3}$, $HL^4$ extracted about 94% of Ag(I) and 3.6% of Cu(II). Similarly, $HL^5$ extracted about 92% of Ag(I) and 5.1% of Cu(II). These results are consistent with the transport results obtained showing that both ligands were selective for Ag(I) and Cu(II), with major preference for Ag(I).

Comparison of the extraction efficiency of $HL^4$ and $HL^5$ for Ag(I) at a ligand concentration of $2 \times 10^{-3}$ mol $dm^{-3}$ shows the order $HL^4 > HL^5$. The extraction efficiency of ligands $HL^4$ and $HL^5$ can also be compared with that of $HL^2$ resulting in the order $HL^4 > HL^5 \cong HL^2$. At a ligand concentration of $2 \times 10^{-3}$ mol $dm^{-3}$, the order of extraction selectivity for Ag(I) compared with Cu(II) is $HL^2 > HL^4 > HL^5$. The percentage extraction results for $HL^4$, $HL^5$ and $HL^2$ are very close to one another. This means that the electron-withdrawing groups ($NO_2^-$ and $Cl^-$) did not result in any discrimination on the extraction behaviour of the ligands.

On the other hand both ligands $HL^6$ and $HL^7$ have electron-releasing methoxy substituents attached to the benzene ring. Both ligands are efficient extraction reagents for Ag(I). Under the conditions employed, consistent with the transport results, the extraction results indicate selective extraction of Ag(I) by both $HL^6$ and $HL^7$. These extraction results are consistent with a 1 : 1 metal : ligand ratio as the actively extracted complex. Although a decrease in the ligand concentration from $2 \times 10^{-3}$ mol $dm^{-3}$ to $1 \times 10^{-3}$ mol $dm^{-3}$ resulted in a decrease in the percentage extraction of Ag(I) by both ligands, the selectivity for Ag(I) was enhanced as would be expected.

The extraction value for ligand $HL^6$ is the same as that for ligand $HL^1$ and the extraction value for ligand $HL^7$ is the same as that for ligand $HL^2$. The following percentage extraction pattern is obtained for ligands $HL^2$, $HL^4$, $HL^5$ and $HL^7$ (which all have diethyl chains), $HL^4 > HL^5 > HL^2 > HL^7$, but all four ligands have roughly the same extraction figure.

The extraction trends show that ligands $H_2L^8$ and $H_2L^9$ are excellent reagents for the liquid–liquid extraction of Ag(I). Under the conditions employed, consistent with the transport results, the extraction results indicate that these ligands are very efficient and selective for Ag(I) extraction compared to the other six metal ions. At a ligand concentration of $2 \times 10^{-3}$ M, 98% of Ag(I) was extracted by $H_2L^8$. When the ligand concentration was decreased to $1 \times 10^{-3}$ mol $dm^{-3}$, the extraction of Ag(I) decreased to 95%. A similar trend and percentages of Ag(I) extraction were obtained with $H_2L^9$.

Comparison of the extraction efficiency of the mono-alkyl substituted acylthioureas with the dialkyl-substituted analogues shows that the former ligands are more efficient and selective for the extraction of Ag(I).

The co-ordination chemistry toward the platinum group metals reviewed by Koch[6] on these ligands indicated that the oxygen atom of the carbonyl group in mono-alkyl substituted acylthioureas is not available for complex formation with metal ions due to intra-molecular hydrogen bonding. Therefore, based on this argument we can expect ligands $H_2L^8$ and $H_2L^9$ to co-ordinate with Ag(I) through only the sulfur donor atom. If this is the case, then we would expect the ligands to extract Ag(I) in a 1 : 1 ligand to metal mole ratio. In other words, $2 \times 10^{-3}$ mol $dm^{-3}$ ($3 \times 10^{-5}$ mol) of the ligand would be theoretically required to extract the total amount of Ag(I) ($1 \times 10^{-2}$ mol $dm^{-3}$, $3 \times 10^{-5}$ mol) in the aqueous phase. However, inconsistent with our expectation, decreasing the ligand concentration to $1 \times 10^{-3}$ mol $dm^{-3}$ had no significant effect on the percentage extraction of Ag(I) by these ligands. However, interestingly, reducing the ligand concentration further to $5 \times 10^{-4}$ mol $dm^{-3}$ resulted in a decrease of Ag(I) extraction almost by half. From the above results, it seems that one mole of the ligand ($H_2L^8$ or $H_2L^9$) is extracting almost two moles of Ag(I). In the absence of more evidence, it is difficult to discuss these results any further.

## The crystal structure for tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) silver(I)] complex

Crystallographic data for the above complex are shown in Table 1. The crystal structure of the tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) silver(I)] complex is shown in Fig. 2. Selected bond lengths and bond angles are listed in Tables 3 and 4, respectively. The structural analysis for this compound shows

**Table 3** Selected bond lengths [Å] for tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) Ag(I)] complex

| Bond | Length/Å | Bond | Length/Å |
|---|---|---|---|
| Ag1–Ag2 | 3.0510(9) | Ag5–Ag6 | 3.0806(9) |
| Ag1–S4 | 2.4616(17) | Ag5–S5 | 2.4266(17) |
| Ag1–O41 | 2.359(4) | Ag5–O81 | 2.342(5) |
| C41–N41 | 1.313(8) | C81–N82 | 1.330(9) |
| C41–S4 | 1.774(6) | C81–S8 | 1.776(8) |
| C42–O41 | 1.242(7) | C82–O81 | 1.231(8) |

**Table 4** Selected bond angles [°] for tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) Ag(I)] complex

| Bond | Angle/° | Bond | Angle/° |
|---|---|---|---|
| Ag1–Ag4–Ag3 | 79.40(3) | Ag5–Ag8–Ag7 | 80.36(3) |
| S1–Ag1–S4 | 148.63(6) | S5–Ag5–S8 | 146.26(6) |
| O11–Ag2–S2 | 122.94(13) | O51–Ag6–S6 | 129.75(12) |
| Ag1–S1–Ag2 | 77.70(5) | Ag5–S5–Ag6 | 77.50(5) |
| C11–S1–Ag1 | 105.1(2) | C51–S5–Ag5 | 105.2(2) |
| C12–O11–Ag2 | 117.3(4) | C52–O51–Ag6 | 124.0(4) |
| C11–N11–C12 | 129.6(6) | C51–N51–C52 | 128.5(6) |
| N11–C11–S1 | 125.0(5) | N51–C51–S5 | 125.7(5) |
| N11–C11–N12 | 118.6(6) | N51–C51–N52 | 117.0(6) |
| O11–C12–N11 | 125.5(6) | O51–C52–N51 | 126.9(6) |
| O11–C12–C13 | 119.4(6) | O51–C52–C53 | 118.7(6) |
| N11–C12–C13 | 115.0(6) | N51–C52–C53 | 114.1(6) |

**Table 5** Average bond lengths [Å] from other structures for comparison

| Complex | $C_s$–S | $C_o$–N | $C_s$–N | $C_o$–O | Ref. |
|---|---|---|---|---|---|
| $Ag_4L_4$ (L = *N*,*N*-diethyl-*N*′-benzoylthiourea) | 1.776 | 1.302 | 1.341 | 1.247 | 30 |
| $AgL_3 \cdot SH$ (L = *N*,*N*-diethyl-*N*′-benzoylthiourea) | 1.681 | 1.381 | 1.417 | 1.218 | 31 |
| $\{AgL^1\}_4$ (L = *N*,*N*-dibutyl-*N*′-benzoylthiourea) | 1.768 | 1.313 | 1.361 | 1.238 | This work |

an empirical formula of $[AgL^1]_4$, forming an interesting cluster.

The ligand $HL^1$ coordinates to Ag(I) in both a mono- and bidentate fashion within the $[AgL^1]_4$ cluster. The nearly squarely orientated silver atoms in this molecule are alternately bonded to each other with sulfur bridges forming an eight-membered ring of alternating silver and sulfur atoms. The bridging sulfur atoms lie above and below the plane through the silver atoms in this configuration. The Ag–Ag separations lie between 2.9687(9) and 3.0949(9) Å and are thus not significantly longer than in metallic silver (2.889 Å). Each Ag atom is co-ordinated to two S- and one O-atom and thus has a co-ordination number of 3. The co-ordination geometry around the silver atom is distorted trigonal as can be seen from the bond angles around each silver atom (see Table 4). The Ag atoms are not in the same plane with the coordinated O and S atoms of the ligands. Ag1 lies 0.0288 Å from the plane defined by S1···S4···O41, Ag2 lies 0.0667 Å from the plane defined by S1···S2···O11, Ag3 lies 0.0462 Å from the plane defined by S2···S3···O21 and Ag4 lies 0.0033 Å from the plane defined by S3···S4···O31.

The ligands co-ordinate as bidentate monoanions. The conformation of the molecule with respect to the thio-carbonyl and carbonyl moieties is definitely twisted as reflected by the torsion angles. The S–Ag–S angles are between 138.27(6) and 148.63 (6)°. The usual Ag–S bond lengths for acylthiourea Ag(I) complexes are in the range 2.45–2.54 Å.[24] In our case, they vary within the ligand chelate rings from 2.457(2) to 2.510(2) Å and are significantly longer than those that do not form part of the ligand chelates [2.399(2) to 2.4304(9) Å]. The Ag–O separations in the chelate rings vary from 2.312(4) to 2.359(4) Å.

Within the chelate rings, there is only partial delocalisation of the bond order. Even though all the C–S, C–O and C–N bond lengths lie between the values for single and double bond order, the C–S separations are longer [1.752(6) to 1.783(7) Å)] compared to those found in other acylthioureas[25–27] and thioamides.[28,29] The C–N distances do not show the usually observed equality and are all shorter than the average single C–N bond length of 1.472(5) Å.[5] They are significantly longer on the acyl side [1.330(9) to 1.392(19) Å] than on the acylthiourea side [1.296(10) to 1.330 (9) Å]. The C–O bond lengths [1.226(7) to 1.249(8) Å)] suggest co-ordination of the oxygen atom.

The C–N bonds between the chelate ring and the amino group [1.330(9) to 1.392(9) Å] show, like in all *N*,*N*-dialkyl-*N*′-acylthioureas and their complexes, partial double bond character in the $C–N(C_4H_9)_2$ group. The phenyl groups are rotated by 9.29(0.87), 8.98(0.64), 3.69(0.47) and 6.04(0.60)° with respect to the planes defined by C12···N11···O11, C22···N21···O21, C32···N31···O31 and C42···N41···O41, respectively.

While the $[AgL^1]_4$ cluster packs with butyl chains in relatively close proximity to one another, there are no direction-specific interactions in this structure. The two crystallographically independent $[AgL^1]_4$ clusters differ most in the conformation of the butyl chains, as might be expected. The determined bond lengths show that the bonding situation of the ligands in the current Ag complex shows a widespread bond delocalisation in the chelate ring.

The bonding mode for the tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) Ag(I)] complex is similar to the one reported earlier for the Ag(I) complex with $HL^2$ ($HL^2$ = *N*,*N*-diethyl-*N*′-benzoylthiourea)[30] but different from the one related structure of a Ag(I) complex reported with *N*,*N*-diethyl-*N*′-benzoylthiourea, $[Ag(HL)_3SH]$.[31] In the latter case, the ligands act as uncharged monodentate sulfur ligands and form a distorted tetrahedral Ag(I) complex in which the bond lengths in the ligands remain largely unchanged upon co-ordination. The fourth co-ordination site is occupied by a hydrogen sulfide ion which is presumably formed from the ligand during complex formation. Similar monodentate sulfur ligand co-ordination to silver through the sulfur atom had also been reported previously.[32] A comparison of the important average bond lengths for the molecular structure of tetra[(*N*,*N*-dibutyl-*N*′-benzoylthiourea) Ag(I)] complex with the previously published Ag(I) complexes with *N*,*N*-diethyl-*N*′-benzoylthiourea is presented in Table 5.

## Conclusion

Under the conditions employed, all the *N*,*N*-dialkyl-*N*′-benzoylthioureas (HL), with the exception of *N*,*N*-di-(2-hydroxyethyl)-*N*′-benzoylthiourea, $HL^3$, were efficient and selective for Ag(I) transport. The *N*-alkyl-*N*′-benzoylthiourea ($H_2L^8$ and $H_2L^9$) ligands were good at transporting Ag(I) into the membrane phase, but not into the receiving phase.

The competitive metal ion extraction results show that all the ligands are very efficient in selectively extracting Ag(I) from a mixture of the seven metal ions. The mono-alkyl substituted aroylthioureas ($HL^8$ and $HL^9$) were not good at transporting Ag(I) or any of the other six metal ions. However, these ligands showed a profound selectivity and efficiency for the extraction of Ag(I).

Finally, the crystal structure of the Ag(I) complex with *N*,*N*-dibutyl-*N*′-benzoylthiourea ligand, $HL^1$, showed interesting monodentate and bidentate co-ordination modes. The structure shows that four silver ions are bound to four molecules of the ligand.

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