

## Determination of Heats of Solvation of Copper(I) and Silver(I) Ions and Halide Complexes in Tetrahydrothiophene

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### Abstract

The heats of solution of the copper(I) and silver(I) halides have been determined in tetrahydrothiophene (THT). THT is a sulfur donor solvent, which coordinates soft metal ions and complexes such as copper(I) and silver(I) strongly. THT has a low dielectric constant, which means that salts rarely dissociate in this solvent. The heats of solvation of the neutral copper(I) and silver(I) halides are obtained by combining the heats of solution and heats of sublimation from the literature. The heats of solvation of the copper(I) and silver(I) ions have been calculated by combining the heats of solution of the neutral metal halides, the heats of complex formation of these complexes, and the heats of solvation of the halide ions in THT. The heats of solvation of the copper(I) and silver(I) ions in THT are  $-698$  and  $-583$   $\text{kJ mol}^{-1}$ , respectively. The obtained heats of solvation show that copper(I) and silver(I) ions and neutral halide complexes are strongly solvated in THT.

### Introduction

In order to determine the heats of solvation of individual ions an extrathermodynamic assumption must be applied. The TATB assumption stating that  $\Delta H_{\text{tr}}^{\circ}(\text{AsPh}_4^+) = \Delta H_{\text{tr}}^{\circ}(\text{BPh}_4^-)$  is the most generally accepted [1, 2] and it has been applied in this study. The heats of solvation of metal ions can be determined from the thermodynamics of formation of the first halide complexes, the heats of solvation of the halide ions, together with the heats of solution of the metal halides. The thermodynamics of complex formation of the copper(I) and silver(I) halides in THT have been studied earlier [3]. Soft metal ions such as silver(I) and copper(I) coordinate the soft sulfur donor solvent THT strongly. In diluted THT solution, two mononuclear complexes are formed, the first one being the strongest. A major desolvation of the metal ion occurs most probably when the second complex is formed [3]. The heats of solvation of the halide ions are determined from the heats of hydration and the heats of transfer [4, 5]. The heats

of solution of the copper(I) and silver(I) halides are measured in this study. These are determined without any extrathermodynamic assumptions, by combining the heat of sublimation and solution both which can be experimentally determined. Heats of solvation of the copper(I) and silver(I) ions, and the copper(I) halides have already been determined in acetonitrile, dimethylsulfoxide and pyridine, and of the silver(I) halides in pyridine [6–9].

### Experimental

#### Chemicals

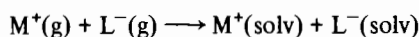
Tetrahydrothiophene (THT) (Fluka 97%) was purified as described elsewhere [10]. The copper(I) halides (Merck p.a.) were recrystallized from acetone and diethylether, kept over phosphorpentoxide at reduced pressure and handled under dry nitrogen. The silver(I) nitrate and sodium halides, used for preparation of the silver(I) halides, were of analytical grade. The silver(I) halides were precipitated from water, carefully washed, dried over phosphorous pentoxide under reduced pressure and kept in dark vessels.

#### Calorimetry

The ampoule calorimeter and procedure used are described elsewhere [11, 12]. Glass ampoules with varying amounts of salt were used in order to check if the heats of solution were dependent on concentration. The ampoules were sealed by melting, and cooled during the sealing. The salts were dissolved within a few minutes in 80 ml of solvent. At least six experiments were performed for each salt. All measurements were performed at  $25.000 \pm 0.002$  °C.

### Calculations

For the reaction



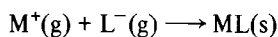
the overall enthalpy change of the two ions M, L is determined by

$$\Delta H_{sv}^{\circ}(M, L) = \Delta H_{sv}^{\circ}(M) + \Delta H_{sv}^{\circ}(L) \quad (1)$$

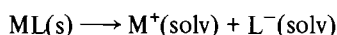
The quantity  $\Delta H_{sv}^{\circ}(M, L)$  is calculated from the heat of solution of the two ions according to

$$\Delta H_{sv}^{\circ}(M, L) = \Delta H_{lat}^{\circ}(ML) + \Delta H_s^{\circ}(ML) - \Delta H_{\beta 1}^{\circ}(ML) \quad (2)$$

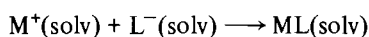
where  $\Delta H_{lat}^{\circ}$  is the lattice enthalpy of  $ML(s)$  in the reaction



$\Delta H_s^{\circ}(ML)$  is the heat of solution of the salt  $ML$



$\Delta H_{\beta 1}^{\circ}(ML)$  is the enthalpy change of the reaction



determined from a calorimetric titration of a metal solution with a solution of the ligand.

The lattice enthalpies  $\Delta H_{lat}^{\circ}(ML)$  at 25 °C for the copper(I) and silver(I) halides are calculated from the standard heats of formation  $\Delta H_f^{\circ}(ML)$ , the heats of sublimation of the metal,  $L_M$ , the heats of atomisation of the halogens,  $D_L$ , the ionisation potentials of the metal ions,  $I_M$  and the electron affinities of the halogen atoms,  $E_L$  according to

$$\Delta H_{lat}^{\circ}(ML) = \Delta H_f^{\circ}(ML) - L_M - D_L - I_M - E_L \quad (3)$$

The heat of solution  $\Delta H_s^{\circ}(M, L)$  is related to the heat of solution of the salt  $ML$ ,  $\Delta H_s^{\circ}(ML)$  by

$$\Delta H_s^{\circ}(M, L) = \Delta H_s^{\circ}(ML) - \Delta H_{\beta 1}^{\circ}(ML) \quad (4)$$

The heat of solvation of the ligand,  $\Delta H_{sv}^{\circ}(L)$  is determined from the heat of hydration and the heat of transfer from water to the solvent according to

$$\Delta H_{sv}^{\circ}(L) = \Delta H_{hydr}^{\circ}(L) + \Delta H_{tr}^{\circ}(L) \quad (5)$$

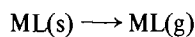
The heat of solvation of the metal ion can be determined in two ways. According to eqn. (1)

$$\Delta H_{sv}^{\circ}(M) = \Delta H_{sv}^{\circ}(M, L) - \Delta H_{sv}^{\circ}(L) \quad (6)$$

or as for the ligand by

$$\Delta H_{sv}^{\circ}(M) = \Delta H_{hydr}^{\circ}(M) + \Delta H_{tr}^{\circ}(M) \quad (7)$$

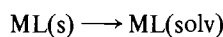
The heat of sublimation  $\Delta H_{sub}^{\circ}(ML)$  from the relation



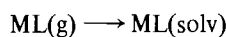
is determined from the coordinate bond energy,  $\Delta H_{CBE}^{\circ}(ML)$  and the lattice enthalpies  $\Delta H_{lat}^{\circ}(ML)$ .

$$\Delta H_{sub}^{\circ}(ML) = \Delta H_{CBE}^{\circ}(ML) - \Delta H_{lat}^{\circ}(ML) \quad (8)$$

The heat of sublimation together with the heat of solution  $\Delta H_s^{\circ}(ML)$  from



gives the heat of solvation of the neutral complex  $\Delta H_{sv}^{\circ}(ML)$  in the reaction



according to

$$\Delta H_{sv}^{\circ}(ML) = \Delta H_s^{\circ}(ML) - \Delta H_{sub}^{\circ}(ML) \quad (9)$$

## Results

The lattice enthalpies,  $\Delta H_{lat}^{\circ}(ML)$  at 25 °C were calculated from the Born–Haber cycle according to eqn. (3). Data used in these calculations are given in Table I. The heats of solution,  $\Delta H_s^{\circ}(ML)$  of the copper(I) and silver(I) halides are negative, Table II. The random errors in  $\Delta H_s^{\circ}(ML)$  were estimated to be less than 2 kJ mol<sup>-1</sup>. The heats of solution were independent of the amounts of salt dissolved for all systems. The heats of solvation of the neutral copper(I) and silver(I) halides, calculated from heats of solution and sublimation, are given in Table III. The

TABLE I. Lattice Enthalpies,  $\Delta H_{lat}^{\circ}$ , for the Reaction,  $M^+(g) + L^-(g) \rightarrow ML(s)$ , Calculated from the Born–Haber Cycle,  $\Delta H_{lat}^{\circ}(ML) = \Delta H_f^{\circ}(ML) - L_M - D_L - I_M - E_L$ . Heat of Sublimation,  $\Delta H_{sub}^{\circ}(ML)$  Calculated from Lattice Enthalpies,  $\Delta H_{lat}^{\circ}(ML)$  and the Coordinate Bond Energy,  $\Delta H_{CBE}^{\circ}$ . According to  $\Delta H_{sub}^{\circ}(ML) = \Delta H_{CBE}^{\circ}(ML) - \Delta H_{lat}^{\circ}(ML)$ . All Values in kJ mol<sup>-1</sup>

ML	$\Delta H_f^{\circ}(ML)^a$	$L_M^b$	$D_L^c$	$I_M^d$	$E_L^e$	$\Delta H_{lat}^{\circ}(ML)$	$\Delta H_{CBE}^{\circ}(ML)^f$	$\Delta H_{sub}^{\circ}(ML)$
CuCl	-136.4	+339.3	+121.8	+745.3	-348.6	-994.2	-756.9	+237.3
CuBr	-105.9	+339.3	+111.7	+745.3	-324.5	-977.7	-750.3	+227.4
CuI	-68.5	+339.3	+106.7	+745.3	-295.3	-964.3	-737.7	+226.6
AgCl	-127.0	+286.2	+121.8	+730.8	-348.6	-917.2	-695.0	+222.2
AgBr	-99.6	+286.2	+111.7	+730.8	-324.5	-903.8	-694.2	+209.6
AgI	-62.3	+286.2	+106.7	+730.8	-295.5	-890.5	-692.5	+198.0

<sup>a</sup>Standard heats of formation of the crystalline halides,  $\Delta H_f^{\circ}(ML)$  for the reaction  $M(s) + 1/2L_2(s, s) \rightarrow ML(s)$ , at 298 K from ref. 15, (s, s) denotes standard state. <sup>b</sup>Heats of sublimation of the metals,  $L_M$ , for the reaction  $M(s) \rightarrow M(g)$ , at 298 K from ref. 15.

<sup>c</sup>Heats of atomization of the halogenes,  $D_L$ , for the reaction  $1/2L_2(s, s) \rightarrow L(g)$ , at 298 K from ref. 16. <sup>d</sup>The ionization potentials of the metal atoms,  $I_M$ , for the reaction  $M(g) \rightarrow M^+(g) + e^-$ , at 0 K from ref. 17.

<sup>e</sup>Electron affinities of the halogen atoms,  $E_L$ , for the reaction  $L(g) + e^- \rightarrow L^-(g)$ , at 0 K from ref. 18. <sup>f</sup>Coordinate bond energies,  $\Delta H_{CBE}^{\circ}$ , at 298 K from ref. 19.

TABLE II. Heats of Solvation of the Neutral Halide Complexes of Copper(I) and Silver(I) in THT Determined from  $\Delta H_s^\circ(\text{ML})$  and  $\Delta H_{\text{sub}}^\circ(\text{ML})$  According to  $\Delta H_{\text{sv}}^\circ(\text{ML}) = \Delta H_s^\circ(\text{ML}) - \Delta H_{\text{sub}}^\circ(\text{ML})$ . All Values in  $\text{kJ mol}^{-1}$

ML	$\Delta H_s^\circ(\text{ML})$	$\Delta H_{\text{sub}}^\circ(\text{ML})^a$	$\Delta H_{\text{sv}}^\circ(\text{ML})$
CuCl	$-41.8 \pm 1.4$	+237.3	-279.1
CuBr	$-48.3 \pm 0.5$	+227.4	-275.7
CuI	$-39.6 \pm 1.5$	+226.6	-266.2
AgCl	$-11.5 \pm 2.0$	+222.2	-233.7
AgBr	$-17.0 \pm 0.9$	+209.6	-226.6
AgI	$-19.4 \pm 0.9$	+198.0	-217.4

<sup>a</sup>The heats of sublimation from Table I.

heats of solution of the two ions,  $\Delta H_s^\circ(\text{M}, \text{L})$  are calculated from  $\Delta H_s^\circ(\text{ML})$  and  $\Delta H_{\beta_1}^\circ(\text{ML})$  according to eqn. (4), Table III. The heats of solvation of the two ions  $\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$  were determined from  $\Delta H_s^\circ(\text{M}, \text{L})$  and  $\Delta H_{\text{lat}}^\circ(\text{ML})$  according to eqn. (2), Table III. Heats of solvation of the halide ions,  $\Delta H_{\text{sv}}^\circ(\text{L})$ , were calculated according to eqn. (5) from  $\Delta H_{\text{hydr}}^\circ(\text{L})$  and  $\Delta H_{\text{tr}}^\circ(\text{L})$  [5]. The  $\Delta H_{\text{sv}}^\circ(\text{L})$  values are  $-341$ ,  $-323$  and  $-311 \text{ kJ mol}^{-1}$  for chloride, bromide and iodide in THT.

Heats of transfer of the halide ions,  $\Delta H_{\text{tr}}^\circ(\text{L})$  have been determined earlier using the TATB assumption, stating that  $\Delta H_{\text{tr}}^\circ(\text{AsPh}_4^+) = \Delta H_{\text{tr}}^\circ(\text{BPh}_4^-)$  [1, 5]. The heats of hydration of the ligands,  $\Delta H_{\text{hydr}}^\circ(\text{L})$  have been determined by Morris [4] employing a calculated heat of solvation of the hydrogen ion,  $\Delta H_{\text{sv}}^\circ(\text{H}^+) = -1103 \pm 13 \text{ kJ mol}^{-1}$ . The errors in  $\Delta H_{\text{sv}}^\circ(\text{L})$  and ultimately in  $\Delta H_{\text{sv}}^\circ(\text{M})$  depend mainly on the errors in  $\Delta H_{\text{hydr}}^\circ(\text{L})$  and  $\Delta H_{\text{sv}}^\circ(\text{H}^+)$ .

Heats of solvation of the copper(I) and silver(I) ions were determined according to eqn. (6) from the heat of solvation of the ligand,  $\Delta H_{\text{sv}}^\circ(\text{L})$ , and the heat of solvation of the two ions,  $\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$ . The values of,  $\Delta H_{\text{sv}}^\circ(\text{M})$  in Table IV determined from the chloride, bromide and iodide salts agree well. The heat of solvation of the copper(I) is  $-698 \text{ kJ mol}^{-1}$

TABLE IV. Heat of Solvation of the Metal Ion,  $\Delta H_{\text{sv}}^\circ(\text{M})$ , in  $\text{kJ mol}^{-1}$  Calculated According to eqn. (6), from  $\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$  in Table III and  $\Delta H_{\text{sv}}^\circ(\text{L})$ , in Table IV

	$\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$	$\Delta H_{\text{sv}}^\circ(\text{L})$	$\Delta H_{\text{sv}}^\circ(\text{M})$	Average
CuCl	-1040.6	-341	-700	
CuBr	-1019.7	-323	-697	
CuI	-1008	-311	-697	-698
AgCl	-923.9	-341	-583	
AgBr	-907.1	-323	-584	
AgI	-892.2	-311	-581	-583

and  $-583 \text{ kJ mol}^{-1}$  for silver(I). The heat of solvation of the metal ion,  $\Delta H_{\text{sv}}^\circ(\text{M})$ , was determined, according to eqn. (7), from the heat of hydration,  $\Delta H_{\text{hydr}}^\circ(\text{M})$ , and the heat of transfer,  $\Delta H_{\text{tr}}^\circ(\text{M})$ . The heat of hydration of the silver(I) ion was determined to be  $-488 \text{ kJ mol}^{-1}$  [13]. The heat of transfer of the silver(I) ion to THT is  $-96.3 \text{ kJ mol}^{-1}$  [5]. The  $\Delta H_{\text{sv}}^\circ(\text{Ag}^+)$  determined from eqn. (7) to be  $-584 \text{ kJ mol}^{-1}$ , agrees very well with  $\Delta H_{\text{sv}}^\circ(\text{Ag}^+)$  of  $-583 \text{ kJ mol}^{-1}$  calculated from  $\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$  and  $\Delta H_{\text{sv}}^\circ(\text{L})$ .

The heat of hydration of the copper(I) has been reported to be  $-607 \text{ kJ mol}^{-1}$  [14]. The heat of transfer from water,  $\Delta H_{\text{tr}}^\circ(\text{Cu}^+)$ , to other solvents has been calculated using this value and the  $\Delta H_{\text{sv}}^\circ(\text{Cu}^+)$  values. The heat of solvation of copper(I) in THT,  $-698 \text{ kJ mol}^{-1}$  gives  $\Delta H_{\text{tr}}^\circ(\text{Cu}^+) = -91 \text{ kJ mol}^{-1}$ , according to eqn. (5).

## Discussion

Tetrahydrothiophene is regarded as a soft donor solvent and it coordinates strongly to soft metal ions such as copper(I) and silver(I). Electrostatic as well as covalent bonding forces between metal ion and solvent molecules contribute to the solvation. The

TABLE III. Heat of Complex Formation,  $\Delta H_{\beta_1}^\circ(\text{ML})$ , Heat of Solution  $\Delta H_s^\circ(\text{ML})$  from Table II, Heat of Solution of the Two Ions,  $\Delta H_s^\circ(\text{M}, \text{L})$ , Lattice Enthalpies,  $\Delta H_{\text{lat}}^\circ(\text{ML})$  from Table I and the Heat of Solvation of the Two Ions,  $\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$ . All values in  $\text{kJ mol}^{-1}$

ML	$\Delta H_{\beta_1}^\circ(\text{ML})^a$	$\Delta H_s^\circ(\text{ML})$	$\Delta H_s^\circ(\text{M}, \text{L})^b$	$\Delta H_{\text{lat}}^\circ(\text{ML})$	$\Delta H_{\text{sv}}^\circ(\text{M}, \text{L})$
CuCl	+4.6	-41.8	-46.4	-994.2	-1040.6
CuBr	-6.3	-48.3	-42.0	-977.7	-1019.7
CuI	+4	-39.6	-44	-964.3	-1008
AgCl	-4.8	-11.5	-6.7	-917.2	-923.9
AgBr	-13.7	-17.0	-3.3	-903.8	-907.1
AgI	-17.7	-19.4	-1.7	-890.5	-892.2

<sup>a</sup>Ref. 3. <sup>b</sup>Calculated according to eqn. (4).

TABLE V. The Heats of Solvation,  $-\Delta H_{sv}^{\circ}$ , in  $\text{kJ mol}^{-1}$ , of Copper(I) and Silver(I) Ions and Halide Complexes in Water (W), Acetonitrile (AN), Dimethylsulfoxide (DMSO), Pyridine (Py) and Tetrahydrothiophene (THT)

	W	AN <sup>c</sup>	DMSO <sup>c</sup>	Py <sup>c</sup>	THT
Cu <sup>+</sup>	607 <sup>a</sup>	679	649	734	698
Ag <sup>+</sup>	488 <sup>b</sup>	529	539	594	583
CuCl		250.2	247.1	303.4	279.1
CuBr		242.7	238.1	293.4	275.7
CuI		232.4	228.1	288.0	265.2
AgCl				235.1	233.7
AgBr				223.8	226.6
AgI				219.7	217.4

<sup>a</sup>Ref. 14.    <sup>b</sup>Ref. 13.    <sup>c</sup>Ref. 9.

degree of covalency in the solvate bond depends on the softness of both the metal ion and the solvent. Silver(I) is somewhat more polarizable than copper(I), and due to the soft character of silver(I) and THT the covalent contribution is expected to predominate. The stronger electrostatic forces of copper(I) make the solvation, in general, stronger than for silver(I), Table V.

The heats of solvation of the neutral copper(I) and silver(I) halide complexes are markedly lower than the heats of solvation of the metal ions, since no charge is neutralized on the neutral complexes. Furthermore, a desolvation takes place when the neutral copper(I) and silver(I) halide complexes are formed [31]. The heat of solvation is strongly dependent on the effective charge on the metal. The effective charge on the metal becomes smaller the more covalent the bonds are within the complex. The iodide complexes have lower values of heat of solvation than the bromide and chloride complexes. The softness of the ligand and the covalency in the metal halide bond increase in the order  $\text{Cl}^- < \text{Br}^- < \text{I}^-$ . The effective charge on the metal thus decreases in the opposite order.

The heats of solvation of the copper(I) and silver(I) ions and halides are larger in pyridine than in THT, Tables IV and V. This is somewhat surprising since the soft acceptor mercury(II) forms markedly stronger bonds to THT than to pyridine [20] and as silver(I) forms complexes with THT in pyridine solution [21]. For sulfur donor solvents, lower heats of solvation than expected from the solvate bond strength have been reported for neutral mercury(II) halide complexes [23]. This is explained by THT and other sulfur donor solvents having a pronounced bulk structure built up by S-S intermolecular interactions. Such S-S interactions have indeed been observed in large angle X-ray scattering studies on THT solutions [23]. This means that much more energy is required to make THT molecules available for solvation, *i.e.*

they are taken out of the bulk structure, than pyridine molecules, due to much stronger intermolecular forces. Pyridine has no pronounced bulk structure since it is built up mainly by van der Waals forces.

The heats of solvation of neutral mercury(II) halides also showed that the bromide complex is more strongly solvated than the other halide complexes in THT, contrary to the other solvents where the heat of solvation increases in the order  $\text{HgI}_2 < \text{HgBr}_2 < \text{HgCl}_2$  [22]. The tendency for an especially strong solvation of bromide complex in THT is also seen for the silver(I) and copper(I) bromide complexes, Table V. It is less striking for the AgBr and CuBr complexes because these contain only one bromide atom. One reason for this behaviour can be that the bromide ion, free or in complexes, fits better into the THT bulk structure and less energy is required for restructuring the bulk than for the smaller chloride ion and the larger iodide ion. This is supported by the stability of the dibromocuprate(I) complex in THT being weaker than the corresponding chloride and iodide complexes [3].

#### Acknowledgement

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#### References

- 1 E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **88**, 2598 (1966).
- 2 B. G. Cox and A. J. Parker, *J. Am. Chem. Soc.*, **95**, 402 (1973).
- 3 M. Johnsson, I. Persson and R. Portanova, *Inorg. Chem. Acta*, **127**, 35 (1987).
- 4 D. F. C. Morris, *Struct. Bonding (Berlin)*, **4**, 63 (1968).
- 5 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, **127**, 25 (1987).
- 6 S. Ahrland, K. Nilsson and B. Tagesson, *Acta Chem. Scand., Ser. A*, **37**, 193 (1983).
- 7 S. Ahrland, P. Bläuenstein, B. Tagesson and D. Tuthar, *Acta Chem. Scand., Ser. A*, **34**, 265 (1980).
- 8 S. Ahrland, S. Ishiguro and I. Persson, *Acta Chem. Scand., Ser. A*, **40**, 418 (1986).
- 9 S. Ahrland and S. Ishiguro, to be published.
- 10 M. Johnsson and I. Persson, *Inorg. Chim. Acta*, **127**, 15 (1987).
- 11 L. Kullberg, *Acta Chem. Scand., Ser. A*, **28**, 979 (1974).
- 12 S. Ahrland, B. Tagesson and D. Tuthar, *Acta Chem. Scand., Ser. A*, **31**, 625 (1977).
- 13 G. R. Hedwig and A. J. Parker, *J. Am. Chem. Soc.*, **96**, 6589 (1974).
- 14 D. R. Rosseinsky, *Chem. Rev.*, **65**, 467 (1965).
- 15 G. N. Lewis and M. Randall, 'Thermodynamics', (revised by K. S. Pitzer, and L. Brewer), McGraw-Hill, New York, 1961, Appendix 7.

- 16 A. G. Sharpe, in V. Gutmann (ed.), 'Halogen Chemistry', Vol. 1, Academic Press, London/New York, 1967.
- 17 'Handbook of Chemistry and Physics', 58th edn., CRC Press, West Palm Beach, 1977-1978, p. E-68.
- 18 R. S. Berry and C. W. Reimann, *J. Chem. Phys.*, **38**, 1540 (1963).
- 19 S. Ahrland, *Struct. Bonding (Berlin)*, **5**, 118 (1968).
- 20 I. Persson, M. Sandström and P. L. Goggin, *J. Chem. Soc., Dalton Trans.*, in press.
- 21 F. Zintl and I. Persson, *Inorg. Chim. Acta*, in press.
- 22 I. Persson, M. Landgren and A. Marton, *Inorg. Chim. Acta*, **116**, 135 (1986).
- 23 M. Johansson and I. Persson, *Inorg. Chim. Acta*, in press.