First Determinations of Complex Formation Constants in Liquid Ammonia Solutions using Potentiometric Titrations: Cyano- and Thiocyanato-silver(I) Complexes at 233 K

Yvonne M. Cheek, Peter Gans,* and J. Bernard Gill*

Department of Inorganic and Structural Chemistry, The University, Leeds LS2 9JT, U.K.

The first stability constant determinations in liquid ammonia solutions for complexation of Ag^+ by CN^- and SCN^- are reported, and the anomalous order of the stepwise constants for the formation of AgCN and $[Ag(CN)_2]^-$ is explained: for (CN^-) $\log K_1 = 7.9 \pm 0.2$, $\log K_2 = 9.1 \pm 0.1$, $\log K_3 = 1.5 \pm 0.4$; (SCN^-) $\log K_1 = 0.7 \pm 0.3$ (mol dm^{-3} units).

We report the first stability constant measurements for metal complexes in liquid ammonia solutions. Potentiometric titrations were carried out in a concentration cell as illustrated.

KCN (or KSCN) (am)
at 3.50×10^{-3} mol dm^{-3}
↓

3 × Ag metal electrodes	$AgNO_3$ (am) $m_1 = 3.50 \times 10^{-4}$ mol dm^{-3} Et_4NNO_3 (am) at 5.00×10^{-2} mol dm^{-3}	$AgNO_3$ (am) $m_2 = 0.700 \times 10^{-2}$ mol dm^{-3} Et_4NNO_3 (am) at 5.00×10^{-2} mol dm^{-3}	2 × Ag metal electrodes

am = liquid ammonia

Solutions of $AgNO_3$ in the working electrode (left compartment) were titrated with solutions of KCN or KSCN. The reference electrode (right compartment) contained a solution of fixed concentration of $AgNO_3$. Both electrode compartments contained the same concentration of tetraethylammonium nitrate as ionic background. The working electrode compartment was fitted with three silver metal electrodes and the reference compartment with two electrodes.

The cell, mounted in a thermostatically controlled cryostat bath at −40 ± 0.05 °C, was mounted in an assembly of standard flasks to enable solutions of accurately known concentrations to be prepared and transferred into the cell compartments.[1,2] Solutions of KCN or KSCN at −40 °C were titrated into the working electrode compartment from a double-jacketted glass burette. Through the inner jacket was pumped coolant liquid from the cryostat bath, whilst the outer jacket was evacuated to a Dewar vacuum to prevent icing. Liquid–liquid contact between the two electrode compartments was made through a low porosity glass sinter fitted within the bore of the key of the tap situated between the cell compartments. The Ag/Ag^+ couple has been proved to be a stable reversible reference electrode for liquid ammonia solutions.[1—3]

The e.m.f. of the concentration cell[1] should be given by expression (1), where t_- is the transference number of the nitrate anion, m_1 and γ_1 are the Ag^+ cation concentration and the mean ionic activity respectively at the working electrode, and a_2 is the Ag^+ ion activity at the reference electrode. The first term is effectively constant because a_2 is held constant throughout the titration, and γ_1 must be assumed to remain constant because of the presence of background electrolyte. The six available electrode pairs were calibrated experimentally against known Ag^+ ion concentrations between 10^{-1} and 10^{-6} mol dm^{-3} at the working electrode.

$$E_{cell}/V = 2RTt_-/F \ln(\gamma_1/a_2) + 2RTt_-/F \ln(m_1) \qquad (1)$$

The measured e.m.f.'s could be conveniently expressed by equation (2), but the slope was not exactly equal to $2RTt_-/F$, and differed for each electrode pair. The stability constants have been calculated with the new SUPERQUAD program[4] using values for the slopes obtained from the calibrations, and subjecting $E_{const.}$ to iterative refinement. This was necessary as $E_{const.}$ was not the same in the titrations as in the calibration experiments.

$$E_{cell}/V = E_{const.} + (\text{slope}) \ln (m_1) \qquad (2)$$

The titration curve shown in Figure 1 illustrates the

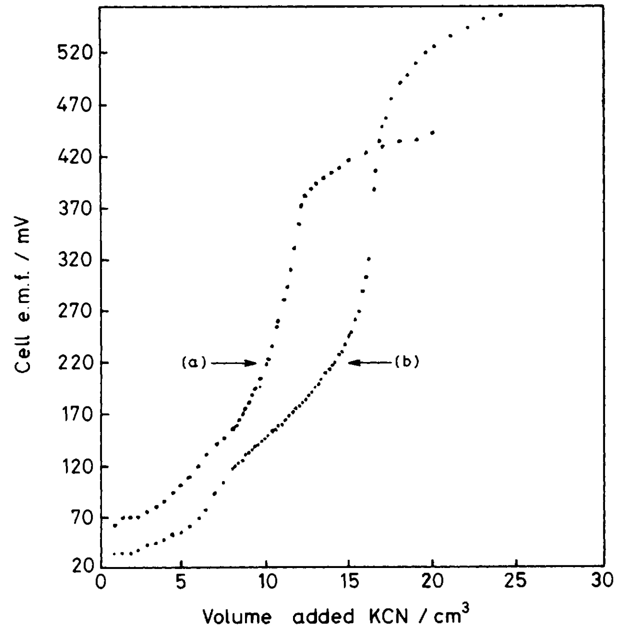

Figure 1. Potentiometric titrations of solutions of 3.50 × 10^{-4} mol dm^{-3} $AgNO_3$ with 3.50 × 10^{-3} mol dm^{-3} KCN in liquid NH_3 at 233 K with (a) 5.00 × 10^{-2} mol dm^{-3} Et_4NNO_3 as background electrolyte, and (b) no background electrolyte.

favourable formation of both the 1 : 1 and 1 : 2 complexes. The Raman spectra also proved the existence of a 1 : 3 species.[5] No inflexion was apparent in the titration curves in the region where $[CN^-]/[Ag^+]$ ~3. However, the change in E_{cell} was greater than could reasonably be accounted for by the dilution effect of adding further KCN titrant beyond the 1 : 2 complexation stage.

The most satisfactory fit of the data using SUPERQUAD gave the following values for the stepwise formation constants: $\log K_1 = 7.9 \pm 0.2$, $\log K_2 = 9.1 \pm 0.1$, and $\log K_3 = 1.5 \pm 0.4$ (mol dm^{-3} units). We believe that evidence in the titration curves for $[Ag(CN)_3]^{2-}$ was not conclusive because of the high stability of the bis complex (at the second equivalence point the calculated concentration m_1 was less than 10^{-9} mol dm^{-3}).

Our second-derivative Raman spectroscopic study[5] of the complexation of Ag^+ by CN^- proved the existence of at least 11 complexed species in the Ag^+/CN^- system. Among others these include the linkage isomeric forms, AgCN, AgNC, $[Ag(CN)_2]^-$, $[Ag(CN)(NC)]^-$, and $[Ag(NC)_2]^-$. Potentiometric titrations do not distinguish between these isomers but see them collectively as 1 : 1 and 1 : 2 species. At the low $[Ag^+]$ concentrations used in the titrations it is unlikely that the ion-aggregated polycationic species detected spectroscopically when $[Ag^+] > 0.5$ mol dm^{-3} will influence the titration results.

That K_1 is less than K_2 can be ascribed to the geometry changes which occur in the co-ordination sphere of the Ag^+ cation between the first and second complexation stages. In the first step one CN^- ligand directly replaces one NH_3 molecule in the solvation sphere of the tetrahedral $[Ag(NH_3)_4]^+$ cation.[6] In the second step the linear $[Ag(CN)_2]^-$ complex, for which there is good spectroscopic evidence,[5] is formed. It is probably the high translational entropic contribution to the free energy change of the second step which gives rise to the anomalously high value of K_2.

Titrations of Ag^+ with SCN^- produced only a very small change in E_{cell} (~5 mV), but a close examination of the data revealed that this occurred at the 1 : 1 end-point. Calculations led to $\log K_{AgSCN}$ ~0.7 ± 0.3 (mol dm^{-3} units) for the formation of AgSCN and were entirely consistent with the Raman spectroscopic titrations of SCN^- on Ag^+ from which it was previously estimated[7] that $\log K_{AgSCN}$ lies in the range 5—20, and that the 1 : 2 complex could be observed only when the $[SCN^-]/[Ag^+]$ ratio is very large (~10).

Received, 11th February 1985; Com. 174

References

1 J. Evans, J. B. Gill, and A. Prescott, *J. Chem. Soc., Faraday Trans. 1*, 1979, 1023.
2 Y. M. Cheek, J. B. Gill, S. Balt, and W. E. Renkema, *J. Solution Chem.*, 1983, **12**, 829.
3 S. Balt and W. de Keviet, *J. Solution Chem.*, 1978, **7**, 915.
4 P. Gans, A. Sabatini, and A. Vacca, *J. Chem. Soc., Dalton Trans.*, in the press.
5 P. Gans, J. B. Gill, M. Griffin, and P. Cahill, *J. Chem. Soc., Dalton Trans.*, 1981, 968.
6 P. Gans and J. B. Gill, *J. Chem. Soc., Dalton Trans.*, 1976, 779.
7 P. Gans, J. B. Gill, and M. Griffin, *J. Chem. Soc., Faraday Trans. 1*, 1978, 432.