Direct Electrochemical Synthesis of Metal Thiocyanate Complexes

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Received January 4, 1985

Electrochemical methods in which a sacrificial metal anode is dissolved into aqueous or non-aqueous electrolytes are an established way of producing various metal complexes, especially halides [1, 2]. Here we report a convenient route to metal thiocyanate complexes, which can be prepared in a single step from the metal using a non-aqueous solution of thiocyanic acid as the electrolyte in a simple cell. The method has been proved by the preparation of solutions of the complex acids $H_2Zn(NCS)_4$ and $H_3Ga(NCS)_6$, and crystalline salts of anionic thiocyanato complexes of zinc, cadmium, gallium, tin, cobalt and gold.

Experimental

Electrolyte

In a typical experiment, 9 ml of 40% aqueous tetrafluoroboric acid, HBF_4, is added to a solution of potassium thiocyanate, 4.0 g, in 100 ml of acetonitrile. Filtration, under nitrogen, through a sintered glass crucible removes the precipitated KBF_4, giving a colourless (or pale pink) solution of the acid HNCS; 20 ml of this solution forms the electrolyte of a cell with a platinum wire cathode and a sacrificial anode consisting of a strip or rod of the particular metal. The cell is similar to that described previously for the preparation of metal halide complexes [1, 2].

Electrolysis with an applied voltage of 2–5 V and a current of 50–200 mA results in the evolution of hydrogen at the cathode and the smooth dissolution of the metal to yield a solution from which thiocyanato complex anions $M(NCS)_n{}^{a-}$ (for Zn, Cd and Co, n = 4 and a = 2; for Au, n = 4 and a = 1; for Ga, n = 4 or 6 and a = 1 or 3) can be recovered by the addition of an alkylammonium thiocyanate $R_4N \cdot NCS$.

The identity of the complex $M(NCS)_n{}^{a-}$ in solution was established by means of the Raman and/or IR spectrum using known bands due to ν(CN) and ν(M–NCS) vibrations [3, 4]. The spectra of crystalline solids were compared with those of known samples prepared by other means or with data from the literature.

The following complexes, all of which are known compounds, were prepared: $(R_4N)_2Zn(NCS)_4$, where R = Me, Et or n-Bu; $(Ph_4P)_2Zn(NCS)_4$; $(R_4N)_2Cd(NCS)_4$, where R = Me or n-Bu; $n\text{-}Bu_4NGa(NCS)_4$; $(R_4N)_3Ga(NCS)_6$, where R = Me or Et; $Et_4NSn(NCS)_5$; $(Me_4N)_2Sn(NCS)_6$; $(Et_4N)_2Co(NCS)_4$; $Et_4NAu(NCS)_4$.

Discussion

A solution of thiocyanic acid in acetonitrile behaves as a moderately strong acid in that the more electropositive metals, *e.g.* zinc, magnesium or aluminum, are readily attacked and dissolve freely. The application of an electrical potential increases the rate of dissolution, and also causes anodic metals which are otherwise attacked only slowly, or not at all, to be converted to the appropriate thiocyanate complexes. Crystalline products can be easily obtained by the addition of a solution of potassium, alkylammonium, or phosphonium thiocyanate, followed by evaporation of the solvent as necessary. The appropriate choice of suitable counter ion and concentration can result in crystalline material separating directly from the solution as the electrolysis proceeds.

Electrochemical oxidation is thus a convenient direct method for the direct synthesis of a variety of thiocyanate complexes, and has the further advantage that one avoids the presence of halide, which is sometimes difficult to remove from products prepared in the usual way by treating a metal halide with thiocyanate.

Acknowledgements

This work was supported in part by Operating Grants (to D. G. T.) from the Natural Sciences and Engineering Council of Canada, and a travel grant from the Minna-James-Heineman-Stiftung of Hannover (to C. O.). Two of us (C. O., M. J. T.) wish to acknowledge sabbatical leaves from our respective universities.

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0020-1693/85/$3.30

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