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ELUCIDATION OF COORDINATION POLYMER STOICHIOMETRY VIA THERMOMETRIC TITRIMETRY

METAL COMPLEXES OF TRITHIOCYANURIC ACID

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ABSTRACT

An attempt has been made to elucidate the stoichiometry of the coordination polymers formed by trithiocyanuric acid with some metals in both dimethyl formamide and aqueous solution. It is possible, using the technique of thermometric titrimetry, to assign stoichiometries to a number of these complexes. In some cases, however, the solid phases that separate are non-stoichiometric. Comparison is made with the stoichiometries of metal complexes of the related ligands, cyanuric acid and melamine as determined via thermometric titrimetry. This technique is shown to be successful and rapid, in contrast with the conventional procedure.

INTRODUCTION

Compounds in which both metal ions and coordinating groups occur as regularly repeating units have been termed "coordination polymers"[1]. The properties, both chemical and physical, of such polymers have been reviewed, *e.g.* ref. 2. There has, however, been no mention of the use of thermometric titrimetry[3] in the elucidation of the stoichiometries of such compounds. This, in spite of the apparent simplicity and rapidity of the technique. The presence of complex species is indicated by discontinuities in a thermogram[3], the experimental yield, which is a plot of volume versus temperature.

In the case of successive formation of two or more complexes, and, where the formation constants differ by at least two orders of magnitude all species will be detected, provided that there is a large enough difference in their heats of reaction. In order to detect all possible species, titrations should be performed in both directions, *i.e.* metal into ligand and *vice versa*. It is possible that, where one complex is formed in the presence of excess ligand and another is formed in the presence of excess metal, that interconversion between the two may be kinetically slow, and thus not observable during the course of the titration. The application of thermometric titrimety to the elucidation of metal complex stoichiometry has been extensively[3–6] reviewed.

The principal method adopted hitherto to determine the stoichiometry of such coordination polymers has been elemental analysis of the complexes. Such a procedure is often lengthy. It requires the preparation of a large number of samples, obtained from solutions of differing molar ratios of ligand to metal, to cover the range of possible stoichiometric compositions. An additional problem occurring in the synthesis of coordination polymers is the presence, in the complexes, of solvent either as end-groups or occluded in the precipitated material. Such end-groups or occluded solvent are detected in any elemental analysis. Solvents which have strong coordinating properties *e.g.* dimethylformamide are usually good solvents not only for the ligands but also for the polymeric species initially formed. Unfortunately these solvents tend to be strongly retained in the precipitated materials either occluded or themselves coordinated to the metal cations.

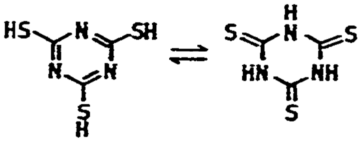

Fig. 1. Trithiocyanuric acid. In the solid state this material exists in the trithione form[26].

Trithiocyanuric acid (TCA), Fig. 1, and its derivatives have received attention almost exclusively in industrial applications, being used, for example, in electroplating baths[7–14], as a cross-linking agent for synthetic rubbers[15,16] and in some photographic processes[17–20]. There has been little other interest in TCA and its metal complexes since they were first reported[21] in 1880. This is surprising in view of its (current) industrial use and additionally the potential semiconducting properties[22] that TCA–transition metal polymers may possess. In the only reports[21,23] on metal–TCA complexes formed in aqueous solution only the physical appearance of the complexes was noted. In most cases further detail, notably analytical data, were omitted. Smolin and Rapaport[24] reviewing, amongst other material, metal–TCA complexes assigned the complexes a 1:1 stoichiometry *e.g.* $C_3HN_3S_3 \cdot M$ where M = Mn, Fe, Co, Ni, Pt, Cu, Au, Zn, Sn, Pb, Bi; the silver complex was designated $C_3HN_3S_3 \cdot Ag_2$. Preliminary elemental analysis, conducted at the commencement of this work, although unsatisfactory for the reasons outlined above, indicated that these assignments were incorrect. For this reason thermometric titrimetry was adopted as a possible technique for the elucidation of the stoichiometries of these complexes.

EXPERIMENTAL

Apparatus

The calorimeter and associated apparatus has been described previously[25]. The only alteration is that the 50 ml beaker has been replaced by a 50 ml capacity silvered dewar vessel.

Materials

Solutions of TCA (0.01, 0.5 and 1.0 *M*) were prepared in dimethylformamide. Similar strength metal acetate solutions were prepared in the same solvent (in some cases 2–3 drops of glacial acetic acid was added to prevent slow precipitation of oxides or basic acetates).

For aqueous solutions the tripotassium salt of TCA was prepared at 0.01, 0.5 and 1.0 *M* concentrations. Similar strength metal solutions were prepared from the respective Analar grade salts. In most cases the maximum concentration of salt attainable was 0.5 *M*.

Cyanuric acid (0.01 *M*) was prepared by dissolution of solid in the minimum of NaOH solution and dilution to the required concentration. Melamine solutions were made by dissolution in water. Both these materials are only sparingly soluble in organic solvents and were therefore not investigated in dimethylformamide solution.

Procedure

Charge the calorimeter with 20 ml of the appropriate solution (molar ratios of titrant to titrand were varied from 1.25 to 5.00). Commence stirring. Fill the Agla all glass syringe (capacity in use 0.50 ml discharged by a synchronous motor in 80 sec) with titrant. Switch on the recorder and obtain a suitable base line[2,5], switch on the burette. Recorder trace yields[3] plot of time (which is equivalent to volume) versus temperature.

RESULTS AND DISCUSSION

Prior to all investigations the contribution of the heats of dilution of the various titrants to the thermogram were recorded. In all cases, except that of the dilution of the tripotassium salt of TCA, these heats of dilution were approximately thermoneutral. The dilution of tripotassium TCA was strongly endothermic, with most metals, however, the heats of reaction were sufficiently large to exceed this dilution effect and the formation of complexes was overall exothermeric.

Table 1 illustrates the results obtained for titrations performed in dimethylformamide and water.

From Table 1 it can be seen that the metal:ligand ratio in the species detected from the thermograms varies considerably. The ideal, fully coordinated polymer structure, shown in Fig. 2a, requires an empirical formula $M_{1.50}L_1$ where M is a divalent metal cation. The table indicates that, in most cases, this structure is not attained during the course of the titration.

In the cases where "irregular" species are indicated the polymerisation process is incomplete; the degree to which it is incomplete is dependent upon the experimental conditions. If the metal is titrated into TCA solution it is to be expected that the species initially precipitated will be deficient in metal, *i.e.* of empirical formula $M_{1.0}L_1$ (as in Fig. 2b). It is also clear that the metal:ligand ratio $M_{0.5}L_1$ can be envisaged if the species shown in Fig. 2c is precipitated.

TABLE I

STOICHIOMETRY OF COMPLEXES FORMED IN SOLUTION AS INDICATED BY BREAKS IN THE THERMOGRAMS[a]

Comment	*Observed in DMF*[b]		*Metal*	*Observed in water*	*Comment*
	metal into TCA	*TCA into metal*			
	not studied		Cr^{3+}	Cr_3L_1	blue-green rather gelatinous ppte, and
				Cr_2L_1	possibly some discontinuities are due to
				Cr_2L_3	the hydrolysis of the chromic ion in the alkaline
				Cr_1L_3	tripotassium salt soln.
no visual change	none		Mn^{2+}	Mn_1L_2	orange-red ppte very small ΔH_R
dark green ppte	$Co_{1.5}L_1$	$Co_{1.6-1.8}L_1$	Co^{2+}	Co_1L_1	intense dark brown soln. On standing, dark green ppte
light green ppte	—	$Ni_{1.5}L_1$	Ni^{2+}	Ni_1L_1	intense dark brown soln. On standing, olive green pptc.
dark brown soln.		$Cu_{1.5}L_1$	Cu^{2+}	$Cu_{1.5}L_1$	red-brown ppte.
Orange ppte after 24 h.	$Cu_{1.5}L_1$	$Cu_{1.3}L_1$			
yellow ppte		Ag_3L_1	Ag^+	Ag_3L_1	yellow ppte
no ppte, Soln. remains clear	$Zn_{2.2}L_1$ $Zn_{1.4}L_1$	$Zn_{2.6}L_1$ $Zn_{1.3}L_1$	Zn^{2+}	Zn_1L_1	pale cream ppte forms after about 0.5 hour
white ppte	$Cd_{1.3}L_1$ $Cd_{1.7}L_1$	$Cd_{1.7-2.0}L_1$	Cd^{2+}	$Cd_{1.2}L_1$	Cream ppte forms after about 0.5 hour
white ppte	$Hg_{1.5}L_1$ $Hg_{3.8}L_1$	Hg_4L_1 $Hg_{1.6}L_1$	Hg^{2+}	not studied	
yellow ppte	$Pb_{1.5}L_1$	$Pb_{1.5}L_1$	Pb^{2+}	$Pb_{1.5}L_1$	yellow ppte
	not	studied	H^+	H_1L_1 H_3L_1	TCA itself ppte

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[a] The TCA molecule less some or all of its protons is represented in the table by L. [b] DMF is an abbreviation for dimethylformamide.

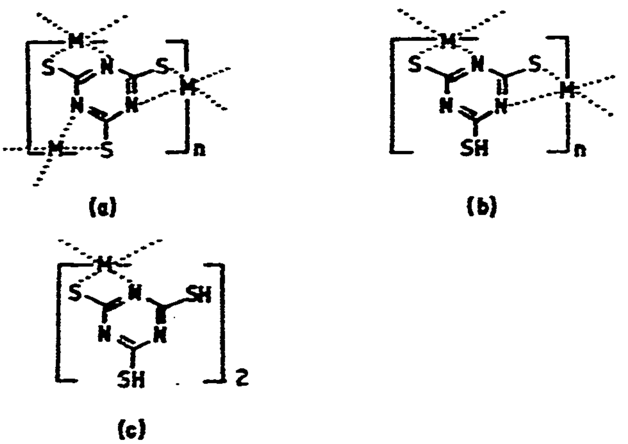

Fig. 2. Metal–TCA structures showing stoichiometries of a) $M_{1.5}L$, b) $M_{1.0}L$ and c) $M_{0.5}L$.

In the reverse situation, *i.e.* TCA titrated into metal, the species expected could be represented as in Figs. 3a and 3b. The ultimate in species deficient in TCA is the dimer shown in Fig. 3b where the metal:ligand ratio is $M_{2.5}L_1$ (Fig. 3a is equivalent to a metal:ligand ratio of 2:1).

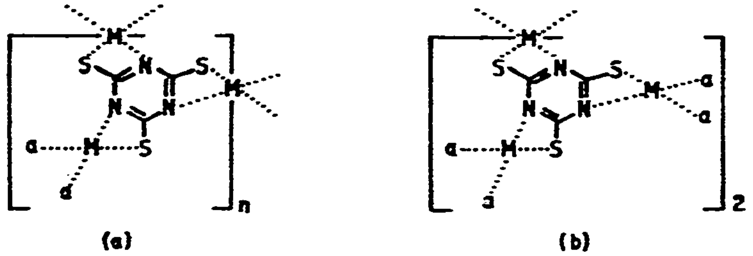

Fig. 3. Metal–TCA structures showing stoichiometries of a) $M_{2.0}L$ and b) $M_{2.5}L$. "a" in the figures represents coordinated solvent molecules.

All the species described by Figs. 2 and 3 have been observed as have several that are intermediate in stoichiometry. All of these structures rearrange towards that shown in Fig. 2a, slowly at room temperature[22], more rapidly on heating but this rearrangement, is, of course, not observeable in the course of a titration. Some thermograms do not have clearly defined discontinuities which points to a whole range of species being formed simultaneously.

Where the discontinuity occurs at, or near to, $M_{1.50}L_1$ the fully polymerised species is formed rapidly, with few of the imperfections mentioned above.

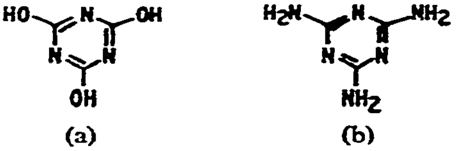

Fig. 4. a, cyanuric acid and b, melamine.

The results of similar investigations into the oxygen and nitrogen (amino) analogues of TCA, respectively cyanuric acid (Ca) (Fig. 4a) and melamine (Fig. 4b) are shown in Table 2.

TABLE 2

Metal	*Species indicated*[a]	*Comment*
Co^{2+}	$Co_{2.9}CA$	pink ppte
Ni^{2+}	Ni_3CA	white ppte
Cu^{2+}	Cu_3CA	light blue ppte
Ag^+	Ag_2CA	white ppte
Zn^{2+}	$Zn_{2.6}CA$	white ppte
Pb^{2+}	$Pb_{3.3}CA$	white ppte

[a] Where CA means cyanuric acid.

Some metal complexes of cyanuric acid have been reported previously (reviewed in ref. 24) but most of the extant work dates from the nineteenth century and would merit reexamination. No discontinuities were observed in titrations with melamine. In the case of both cyanuric acid and melamine titrations were possible in only one direction, *i.e.* metal into ligand because of the low solubility of both ligands in aqueous solution. From the thermograms complexes of the type $M_3Ca \cdot xH_2O$ are indicated under the conditions of the titrations. Heats of reaction are much smaller than those observed with TCA making the thermograms rather flat and discontinuities not clearly defined. This points to weak complexes of the type shown in Fig. 5, further coordination and polymerisation in the manner of TCA does not take place.

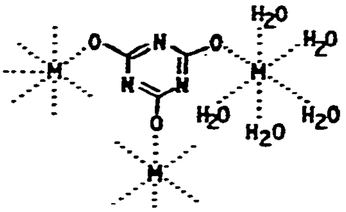

Fig. 5. Metal-cyanuric acid structure showing stoichiometry of $M_{3.0}$cyanuric acid.

CONCLUSIONS

The work described here has indicated the stoichiometries of polymeric species precipitated from solutions of metals and trithiocyanuric acid and cyanuric acid. The conditions defined by these titrations have been used to prepare several of the polymers and investigations on their properties have been carried out. In many cases elemental analysis has confirmed the stoichiometry assigned on the basis of thermometric titrimetry alone. A further paper will describe the preparation and properties of these polymers. Meanwhile thermometric titrimetry has demonstrated its utility in the rapid assignment of stoichiometry and the definition of experimental conditions for the preparation of a range of coordination polymers.

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