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Complex Formation by Dithionate(V) Ion†

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Complexes of dithionate(V) ion with several cations are obtained as the solid potassium salts; in solution, stabilities are less than the corresponding oxalato complexes.

Dithionic acid, the oxoacid of sulfur(V), has been known for some time and has moderate stability at ordinary temperatures.[1] The free acid has not been isolated, although moderately concentrated solutions can be prepared. Many salts of the anion $S_2O_6^{2-}$ are known, and there are reports of its functioning as the counter-ion with cationic complexes formed by other ligands. On a few occasions, a single dithionate ion enters the coordination sphere, with[2] Co in $[Co(NH_3)_5{\cdot}S_2O_6]Cl$ and $K_4[Co(CN)_5{\cdot}S_2O_6]{\cdot}6H_2O$, and with Cr in $[Cr(NH_3)_5{\cdot}S_2O_6]^+$ salts,[3] also[4] in *cis*$[CrL_2F(S_2O_6)]$ where L is either 1,2-diaminoethane or 1,3-diaminopropane.

In some ways, the dithionate(V) ion may be compared with the oxalate ion $C_2O_4^{2-}$ which is known to function as a chelating ligand in the formation of numerous complexes. In aqueous solutions, chelating ligands are known generally to form more stable complexes than the corresponding monodentate ligands, and this suggests that chelate complex formation might take place between some cations and the dithionate(V) ion.

We now report the preparation and characterisation of a number of dithionate(V) complexes, isolated as the potassium salts, together with estimates of stability in solution for three such complexes.

Experimental

Calcium dithionate and barium dithionate were obtained as described.[5] By treatment of their solutions with solutions containing calculated amounts of sulfuric acid or potassium sulfate, followed by separation of precipitated sulfate, the free acid and potassium salt were obtained in solution. For studies of stability constants, the sodium salt was obtained similarly and recovered by evaporation.

To obtain complexes, appropriate amounts of precipitated hydroxides or carbonates of metallic elements were dissolved in the free acid solution, and the potassium salt solution added. After filtration, products were obtained by evaporation to small bulk and crystallisation on cooling. (The aluminium compound was obtained by dissolving aluminium turnings in potassium hydroxide solution, with subsequent addition of an appropriate amount of free acid.)

Characterisation was usually achieved by thermogravimetric analysis over the temperature range 50–400 °C, and sometimes confirmed by volumetric methods, using either oxidation with dichromate for determination of the dithionate ion, or EDTA for divalent cations. The compounds obtained from preparations as above are listed in Table 1 together with the results of thermogravimetric analysis.

Stabilities in Solution.—Experimental estimates of stability constants (log β_2) were made for complex formation with Ni, Zn and Cd by potentiometric titration in a background of sodium perchlorate at 1.0 mol dm^{-3}, and at 24 °C, by the following procedure. To a solution (100 cm^3) in $NaClO_4$ of the appropriate element at 0.002 mol dm^{-3} as sulfate or nitrate was added a solution of sodium dithionate [0.25 mol dm^{-3} (in $NaClO_4$)]. A cleaned metal electrode of the element concerned was immersed in the solution and its potential was measured relative to a saturated calomel electrode between successive additions of dithionate solution up to a mole ratio of 50:1. Reliability of electrode behaviour was confirmed by consistencies within a series of readings, and between titration runs.

Results and Discussion

Solid dithionate(V) salts when heated decompose to the corresponding sulfates with loss of sulfur dioxide. With hydrated salts and complexes, it is often possible to distinguish two separate stages. For example with $CaS_2O_6{\cdot}4H_2O$ losses take place (*a*) between 120 and 200 °C and (*b*) between 250 and 320 °C, corresponding to loss of water and sulfur dioxide respectively.

On this basis, it has been possible in Table 1 to match formulae to the results from thermogravimetric analysis. Close parallels are shown with corresponding oxalato complexes, for example with copper(II);[1] *cf.* $Na_2[Cu(C_2O_4)_2]{\cdot}2H_2O$. For the Ti and Zr complexes, inclusion of oxo or hydroxo groups is necessary to account for the analytical results; *cf.* the ion[6] $[Zr(C_2O_4)_2(OH)_2(H_2O)_2]^{2-}$.

From the potentiometric measurements at excess dithionate, values for log β_2 have been obtained by methods of iterative calculation. Dithionic acid is a strong acid, and the known[7] value of pK_a makes it possible to discount possibilities of protonation of the mononuclear complex species in the conditions pertaining.

Table 1 Thermogravimetric analysis of dithionate(V) complexes

	Loss of mass (%)[a]					
	First stage		Second stage		Overall	
Compound	f	r	f	r	f	r
$K_2Be(S_2O_6)_2$	—	—	—	—	31.3	31.4
$K_3Ce(S_2O_6)_3$	—	—	—	—	25.9	26.1
$K_2Ti(OH)_2(S_2O_6)_2{\cdot}1.6H_2O$	11.0	10.9	26.3	25.2	37.3	36.1
$K_2Zr(OH)_2(S_2O_6)_2{\cdot}2H_2O$	6.4	6.4	25.6	26.1[b]	32.0	32.5
$K_2Ni(S_2O_6)_2{\cdot}6H_2O$	19.0	19.1	22.6	22.7	41.5	41.8
$K_2Cu(S_2O_6)_2{\cdot}2H_2O$	7.0	7.2	25.5	25.7	32.5	32.9
$K_2Zn(S_2O_6)_2{\cdot}4H_2O$	13.5	14.5	24.4	23.9	37.9	38.4
$K_3Al(S_2O_6)_3{\cdot}3H_2O$	—	—	—	—	36.4	36.3

[a]f = found; r = formula requirement; [b]Corresponds with water from $(OH)_2$ in the second stage.

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Values found for log β_2 are: Ni, 4.70 ± 0.7; Zn, 2.40 ± 0.1; Cd, 2.46 ± 0.1, and these may be compared with the range of values listed[7] for the corresponding bis-oxalato complexes: Ni, 7.6–7.9; Zn, 7.6; Cd, 4.1–5.4. They indicate a generally lower stability for the complexes of the dithionate(v) ion.

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References

1 N. V. Sidgwick, *The Chemical Elements and their Compounds*, Oxford, 1950, vol. II, pp. 940–942; M. Schmidt and W. Siebert, in *Comprehensive Inorganic Chemistry*, ed. J. C. Bailar, Pergamon Press, Oxford, New York, 1973, vol. 2, pp. 877–878.
2 M. Calvet, *Afinidad*, 1981, **38**, 131.
3 J. M. Coronas and J. Casabo, *An. Quim.*, 1974, **70**, 335.
4 J. Ribas, J. Casabo and M. D. Baro, *Thermochim. Acta*, 1981, **47**, 271.
5 R. Pfanstiel, *Inorg. Synth.*, 1946, **2**, 167.
6 *Dictionary of Inorganic Compounds*, ed. J. E. Macintyre, Chapman and Hall, London, 1992.
7 *Stability Constants*, The Chemical Society, London, Special Publications No. 17, 1964, pp. 360–364 and 25 (Supplement No. 1), 1971, pp. 245–250.