

USE OF COPPER SALTS OF ARYLSULPHONIC ACIDS IN THE STUDY OF COORDINATION COMPOUNDS*

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The use of copper(II) chloride in the formation of coordination compounds often leads to variations of constitution, particularly in the case of bidentate chelate complexes. Instead of obtaining a dichloride salt in which two molecules of the chelate are coordinated to a copper atom, i.e. $[\text{Cu chel}_2]\text{Cl}_2$, two chlorine atoms may be bound directly to the copper atom to give a neutral complex, $\text{CuCl}_2 \text{chel}$. On the other hand, a tetrachlorocuprate salt, having the same empirical formula but twice the molecular weight is often formed.¹⁻⁴ The use of copper(II) perchlorate⁴ cannot reliably overcome this ambiguity, as perchlorate coordination is known⁵ to occur occasionally. The formation of complex fluoroborates⁶ is usually satisfactory, but these compounds, like the complex perchlorates, are highly insoluble and do not lend themselves readily to recrystallization techniques.

Both these defects can be overcome by the use of organic anions. A study of the coordination complexes of ethylenediamine (en), 2,2'-dipyridyl (dipy), and 1,10-phenanthroline (phen) has been carried out using copper(II) salts of benzenesulphonic acid (bsH), *m*-nitrobenzenesulphonic acid (nbsH), and *p*-toluenesulphonic acid (tsH), and the resulting compounds are listed in Table 1. There is no evidence for coordination of the sulphonate groups in these complexes. All the complexes were prepared by the reaction of hot ethanolic solutions of the appropriate sulphonate and chelate. The benzenesulphonates are sparingly soluble in ethanol and can easily be recrystallized from this solvent, behaving like more normal organic compounds. The ethanol solubilities of the *m*-nitrobenzenesulphonates and *p*-toluenesulphonates increase in that order, and the latter were obtained by addition of ether. All complexes are soluble in water and insoluble in ether, benzene, and acetone.

Considerable flexibility can thus be achieved by the use of organic anions, such as sulphonates. Benzenesulphonates are very useful in the isolation of complex

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¹ Donnan, F. G., Bassett, H., and Fox, C. J. J., *J. chem. Soc.*, 1902, **81**, 939.

² Sidgwick, N. V., "The Chemical Elements and their Compounds." pp. 161-3. (Oxford University Press: London 1950.)

³ MacDermott, T. E., *Aust. J. Chem.*, 1966, **19**, 2389.

⁴ Goodwin, H. A., and Lions, F., *J. Am. chem. Soc.*, 1960, **82**, 5013.

⁵ Barker, N. T., Harris, C. M., and McKenzie, E. D., *Proc. chem. Soc.*, 1961, 335; Harris, C. M., and McKenzie, E. D., *J. inorg. nucl. Chem.*, 1961, **19**, 372; Hathaway, B. J., and Underhill, A. E., *J. chem. Soc.*, 1961, 3091.

⁶ Stratton, W. J., and Busch, D. H. *J. Am. chem. Soc.*, 1958, **80**, 1286.

cations, by virtue of their readiness to submit to recrystallization, whereas the *p*-toluenesulphonates lend themselves readily to kinetic and other solution studies. These anions also contribute characteristic infrared absorptions which assist in

TABLE 1
COPPER(II) COMPLEX SULPHONATES OF ETHYLENEDIAMINE, 2,2'-DIPYRIDYL,
AND 1,10-PHENANTHROLINE

Compound	Colour	C (%)		H (%)		Cu (%)	
		Found	Calc.	Found	Calc.	Found	Calc.
[Cu en ₂]bs ₂	violet	39.2	38.6	5.4	5.3	16.1	16.1
[Cu en ₂]nbs ₂	violet	33.0	32.7	4.1	4.1	10.9	10.8
[Cu en ₂]ts ₂	violet	41.1	41.1	5.7	5.7	11.9	12.1
[Cu dipy ₂]bs ₂	light blue	55.6	55.7	3.8	3.8	9.0	9.2
[Cu dipy ₂]nbs ₂	light blue	49.3	49.3	3.3	3.1	8.1	8.2
[Cu dipy ₂]ts ₂ , $\frac{1}{2}$ H ₂ O	light blue	56.3	56.1	4.3	4.3	8.8	8.7
[Cu phen ₂]bs ₂	light green	58.5	58.6	3.4	3.5	8.3	8.6
[Cu phen ₂]nbs ₂ , $\frac{1}{2}$ H ₂ O	light blue	51.7	51.6	3.1	3.0	7.5	7.6
[Cu phen ₂]ts ₂ , H ₂ O	pale green	57.8	58.2	3.9	4.1	8.1	8.1

TABLE 2
INFRARED DATA OF COPPER(II) COMPLEX SULPHONATES OF
ETHYLENEDIAMINE, 2,2'-DIPYRIDYL, AND 1,10-PHENANTHROLINE
 ν_{\max} in cm⁻¹

Compound	H ₂ O	N-H	C=N and C=C		C-NO ₂
[Cu en ₂]bs ₂	—	3290	—	—	—
		3230			
[Cu en ₂]nbs ₂	—	3290	—	—	1525
		3230			1335
[Cu en ₂]ts ₂	—	3290	—	—	—
		3230			
[Cu dipy ₂]bs ₂	—	—	1590	1560	—
[Cu dipy ₂]nbs ₂	—	—	1595	1565	1525
					1335
[Cu dipy ₂]ts ₂ , $\frac{1}{2}$ H ₂ O	3400	—	1600	1565	—
[Cu phen ₂]bs ₂	—	—	1625	1600	—
				1580	
[Cu phen ₂]nbs ₂ , $\frac{1}{2}$ H ₂ O	3450	—	1625	1600	1525
				1590	1340
[Cu phen ₂]ts ₂ , H ₂ O	3400	—	1620	1600	—
				1580	

the identification of the complexes. All complexes exhibited strong absorption at 1200–1100 cm⁻¹ as a consequence of the sulphonate group. A summary of other important absorption bands is given in Table 2.

Experimental

Analyses

Carbon and hydrogen analyses were performed by Miss B. Stevenson, University of Sydney, and the Australian Microanalytical Service, Melbourne.

Infrared Spectra

Samples were prepared as Nujol mulls and spectra were measured on a Perkin-Elmer Infracord.

Copper(II) Sulphonates

These compounds were prepared by treating copper(II) carbonate with the appropriate sulphonic acid in water, under reflux. Unchanged copper(II) carbonate was removed by filtration and the aqueous filtrate evaporated to give the required compound.

Copper(II) Complexes

These compounds were prepared by addition of a solution of the copper(II) sulphonate in ethanol to a hot solution of the appropriate ligand in ethanol. The complex benzenesulphonates precipitated immediately on cooling and were recrystallized from ethanol. The complex *m*-nitrobenzenesulphonates crystallized after concentration of the reaction solution, followed by cooling and the complex *p*-toluenesulphonates were precipitated by the addition of ether to the concentrated, cooled reaction solution.

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