Some Metal Sulphamates and their Complexes with Diamines and Pyridine. Evidence for Ambidentate Behaviour and Linkage Isomerism of the Sulphamate Group

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A range of metal sulphamates has been prepared and characterised by i.r. and visible spectra and magnetic moments. In $[M(H_2O)_4(NH_2SO_3)_2]$(M = Zn, Co, or Ni) the sulphamate group is co-ordinated *via* oxygen. On elimination of water, co-ordination *via* the amino-group occurs, as demonstrated by i.r. spectroscopy. $[Cr(H_2O)_3(NH_2SO_3)_3]$ Involves *N*-co-ordinated sulphamate. Two forms of copper sulphamate have been prepared involving N- and O-linked sulphamate groups. The N-bonded sulphamatocopper(II) species undergoes ready decomposition to the sulphate complex. Several complexes of metal sulphamates with ethylenediamine, other diamines, and pyridine have been prepared. $[Ni(mepn)_2(NH_2SO_3)_2]$ Is diamagnetic, square planar, but all other Ni^{II} species are of octahedral or tetragonally distorted octahedral stereochemistry. The electronic spectrum of the D_{4h} species $[Ni(py)_4(NH_2SO_3)_2]$ has been studied in detail and parameters calculated *via* a spectrum-fitting procedure. This shows the sulphamate group to be oxygen linked, a conclusion confirmed by i.r. spectroscopy. The other sulphamates $[M(py)_4(NH_2SO_3)_2]$ are also O-linked, except for $[Cu(py)_4(NH_2SO_3)_2]$ which is N-bonded. Some ethylenediamine complexes of copper(II) sulphamate and aminomethanesulphonate are also reported.

As part of a general study on the chemistry of the sulphamate † group, we have investigated its reactivity when co-ordinated to a metal and in this context have prepared a number of sulphamato-complexes which are reported in this paper. Previous examples of sulphamato-complexes include those of the platinum metals [1,2] and the sulphamatopenta-ammine complexes of cobalt-(III) [3] and ruthenium(III).[4] The group is usually regarded as N-bonded to the metal, but the linkage isomer has been postulated [5] as an intermediate in the hydrolysis in aqueous solution of the ion $[Co(NH_3)_5(NH_2SO_3)]^{2+}$. The preparation and thermal decomposition of many metal sulphamates have been reported.

EXPERIMENTAL

Preparation of Metal Sulphamates.—These compounds were prepared by adding a metal carbonate (or oxide or hydroxide) in small portions to an aqueous solution of sulphamic acid until a residue remained. The filtrate was evaporated on a steam-bath, the resulting residue being triturated with acetone when cool until a crystalline solid was formed. This was recrystallised from water. In a few cases the metal sulphamate was prepared by adding sulphamic acid to an aqueous solution of the metal perchlorate in the stoicheiometric ratio, and then reducing the volume of solution until a solid precipitated out. The product was recrystallised repeatedly from water. These methods gave metal sulphamates having water of crystallisation (usually 4 mol). The anhydrous form was obtained by heating *in vacuo*. Several examples were deuteriated by recrystallisation from D_2O.

Preparation of Complexes of Metal Sulphamates.—This preparation was attempted for Ni^{II}, Co^{II}, Cu^{II}, and Zn^{II}. 1 : 4 Pyridine complexes were prepared by adding a fourfold excess of pyridine to solutions of nickel(II) or cobalt(II) sulphamates and to a suspension of copper(II) sulphamate in methanol. Precipitation occurred rapidly. The metal sulphamates had previously been stirred for several hours in 2,2′-dimethoxypropane. The complexes were recrystallised from methanol. Other pyridine complexes (of 1 : 1 stoicheiometry) were prepared by thermal decomposition. Ethylenediamine complexes were prepared by adding the ligand in 1 : 2 and 1 : 3 molar ratios to the metal sulphamates as described for pyridine except that the preparation with copper(II) sulphamate was carried out in the minimum volume of water. The preparation of complexes of nickel(II) sulphamate with a number of diamines and tetra-amines was attempted in order to extend studies being carried out in this department [6] [1,3-diaminopropane (pn), 1,2-diamino-2-methylpropane (mepn), 1,4,8,11-tetra-azaundecane, and 1,5,8,12-tetra-azadecane]. 1 : 2 Complexes were prepared with pn and mepn using methanol as a solvent and reactants in 1 : 2 molar ratios, but while complexes with the remaining ligands were formed in solution they could not be isolated.

Preparation of Metal Derivatives of Other Aminosulphonic Acids. This preparation was attempted without much success. The compound $Cu[NH_2CH_2SO_3]_2$ was prepared by literature methods [7] and $[Cu(en)_2(NH_2CH_2SO_3)_2]\cdot 2H_2O$

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† According to the I.U.P.A.C. rules for the Nomenclature of Inorganic Compounds the group is correctly called the sulphamidato-group.

[1] W. P. Griffith and D. Pawson, *J.C.S. Dalton*, 1973, 524.

[2] L. Ramberg and S. Kallenberg, *Ber.*, 1912, **45**, 1512; H. Kirmreuther, *ibid.*, 1911, **44**, 3115; V. V. Lebedinskii, *Izvest. Inst. Plat.*, 1947, **194**, 99.

[3] L. P. Po and R. B. Jordan, *Inorg. Chem.*, 1968, **7**, 526.

[4] J. N. Armor and H. Taube, *Inorg. Chem.*, 1971, **10**, 1570.

[5] E. Sushynski, A. Van Roodselaar, and R. B. Jordan, *Inorg. Chem.*, 1972, **11**, 1887.

[6] T. J. Barton and R. J. Slade, unpublished work.

[7] G. Palmer, ‘ Experimental Inorganic Chemistry,’ Cambridge University Press, Cambridge, 1954.

obtained by the addition to it of ethylenediamine in 2 : 1 ratio. The compound $Cr[NH_2CH_2SO_3]_3$ was the only other metal derivative of aminomethanesulphonic acid that could be isolated, while no success was achieved with taurine ($NH_2CH_2CH_2SO_3H$). All compounds were characterised by C, H, N, and metal analyses as appropriate (Table 1). The complexes of the metal sulphamates absorbed water readily, but they were thoroughly dried before any measurements were carried out on them.

Instrumentation.—I.r. spectra were measured on a Perkin-Elmer 325 spectrometer (4 000—200 cm^{-1}) using Nujol/hexachlorobutadiene mulls and NaCl or CsI plates. Solid-state reflectance spectra were recorded on a Unicam SP 700 spectrometer fitted with an SP 735 attachment or on a Beckmann DK 2A instrument, on which all low-temperature spectra were measured. Magnetic moments were measured at room temperature and over a temperature range by the Gouy method (Newport Mk II). Thermal analysis was carried out on a Stanton–Redcroft thermobalance, model TR, and conductivity studies on a Doran bridge, with 10^{-3}M-solutions.

TABLE 1

Analytical data (%)

Compound	Colour	Calc. C	Calc. H	Calc. N	Found C	Found H	Found N
$Ag[NH_2SO_3]$	White		1.41	6.86		1.45	7.0
$Cu[NH_2SO_3]_2\cdot 2H_2O$	Blue [a]		2.74	9.61		2.85	9.2
$Cu[NH_2SO_3]_2\cdot 3H_2O$	Blue [b]		3.23	9.06		3.1	9.1
$Cu[NH_2SO_3]_2\cdot 2H_2O$	Green		2.74	9.61		2.7	9.5
$Ni[NH_2SO_3]_2\cdot 4H_2O$	Green-blue		3.72	8.68		3.75	8.75
$Ni[NH_2SO_3]_2\cdot 2H_2O$	Yellow		2.81	9.80		2.85	10.3
$Co[NH_2SO_3]_2\cdot 4H_2O$	Pink		3.72	8.68		3.8	9.05
$Co[NH_2SO_3]_2\cdot 2H_2O$	Purple		2.84	9.76		2.7	9.65
$Cr[NH_2SO_3]_3\cdot 4H_2O$	Dark green		3.40	10.2		3.45	10.1
$Cr[NH_2SO_3]_3\cdot 3H_2O$	Dark green		3.05	10.4		3.2	10.6
$Ba[NH_2SO_3]_2\cdot H_2O$	White		1.73	8.05		1.75	8.25
$Zn[NH_2SO_3]_2\cdot 4H_2O$	White		3.65	8.52		3.65	8.8
$[Ni(en)_3(NH_2SO_3)_2]$	Purple	16.7	6.50	26.0	16.7	6.5	27.2
$[Ni(en)_2(NH_2SO_3)_2]\cdot H_2O$	Blue	12.4	5.80	22.6	12.5	5.9	22.1
$[Ni(mepn)_2(NH_2SO_3)]\cdot 2H_2O$	Yellow	21.6	6.10	18.9	21.7	6.3	19.8
$[Ni(pn)_2(NH_2SO_3)_2]\cdot 3H_2O$	Lilac	15.9	6.61	18.5	15.9	6.1	17.2
$[Ni(py)_4(NH_2SO_3)_2]\cdot 2H_2O$	Blue	39.8	4.40	13.8	39.8	4.4	13.7
$[Co(en)_3(NH_2SO_3)_2]$	Pink	16.7	6.50	26.6	16.7	6.35	25.0
$[Co(py)_4(NH_2SO_3)_2]$	Pink	42.3	4.23	14.8	41.9	4.3	14.7
$[Zn(en)_3(NH_2SO_3)_2]$	White	15.2	6.76	23.7	15.5	6.95	24.6
$[Zn(en)_2(NH_2SO_3)_2]$	White	12.7	5.38	22.2	12.9	6.1	22.3
$[Cu(py)_4(NH_2SO_3)_2]\cdot 4H_2O$	Blue	37.3	4.97	13.0	37.2	5.05	12.6
$[Cu(en)_2(NH_2SO_3)_2]\cdot H_2O$	Purple	12.2	5.50	21.3	12.2	5.4	20.3

[a] Prepared from $CuCO_3$: Cu; found 21.7%, calculated 21.8%. [b] Prepared from $Cu[ClO_4]_2$: Cu; found 19.6%, calculated 20.4%.

RESULTS AND DISCUSSION

Metal Sulphamates.—These compounds are listed in Table 1. Some have been prepared before, but we have reprepared them for comparison purposes. In any case few systematic studies have been carried out on them apart from work [8] on their i.r. spectra (to 500 cm^{-1}) and their thermal decomposition.[9-11] In general they decompose to sulphate, sometimes *via* intermediate imidodisulphonate species. We have carried out the dehydration of aquametal sulphamates at temperatures well below those necessary for sulphate formation. The loss of water occurred with colour changes in the case of the transition-metal sulphamates. Nickel(II) and cobalt(II) sulphamates crystallised initially as $[M(H_2O)_4(NH_2SO_3)_2]$, being blue-green and pink respectively. Their magnetic moments and electronic spectra (Table 2) are typical of octahedral complexes. The spectrum of the Ni^{II} species shows no splitting due to symmetry lower than O_h, but some splitting is seen in the lowest energy band in the spectrum of the cobalt compound. In the latter case it is of interest to note the absorption at 16.4 kK * [as a shoulder on the $^4T_{1g} \longrightarrow {}^4T_{1g}(P)$ band] which we assign to the $^4T_{1g} \longrightarrow {}^4A_{2g}(F)$ transition. Both sulphamates lost 2 mol of water on heating (with correct weight loss) giving yellow $Ni[NH_2SO_3]_2\cdot 2H_2O$ and purple $Co[NH_2SO_3]_2\cdot 2H_2O$ both of octahedral stereochemistry. The electronic spectrum of the Ni^{II} species shows a split $^3A_{2g} \longrightarrow {}^3T_{2g}$ band, indicating some distortion. The absorption bands shift to lower energy in the diaqua-complex compared to the tetra-aqua-species. On further heating the anhydrous sulphamates are formed without colour change.

The copper(II) sulphamates proved to be of interest. The blue compound $Cu[NH_2SO_3]_2\cdot 2H_2O$ (prepared from sulphamic acid–$CuCO_3$), underwent a colour change to emerald green at 180 °C with the loss of 1 mol of water, which was eventually taken up again without colour change. Both blue and green forms show one broad band in the visible spectrum, have normal moments, and appear to be six-co-ordinate species. The blue product $Cu[NH_2SO_3]_2\cdot 3H_2O$ (prepared from $Cu[ClO_4]_2$–sulphamic acid) readily loses 1 mol of water giving $Cu[NH_2SO_3]_2\cdot 2H_2O$ which gives a white anhydrous product when

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* $1kK = 10^3\ cm^{-1}$.

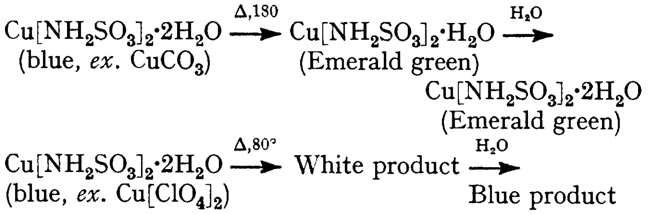
[8] L. Bicelli and A. La Vecchia, *Ann. Chim.* (*Italy*), 1956, **46**, 661; 1957, **47**, 1380.

[9] M. Capestan, *Ann. Chim.* (*France*), 1960, **5**, 207.

[10] S. Sampath and G. Aravamudan, *Indian. J. Chem.*, 1971, **9**, 1282.

[11] C. Rocchiccoli, *Compt. rend.*, 1962, **255**, 1942; *Ann. Chim.* (*France*), 1960, **5**, 999.

heated to 80 °C. The blue colour is reformed in air with the uptake of water. This behaviour is similar to that of copper(II) sulphate, and provides a noteworthy difference between the two forms of $Cu[NH_2SO_3]_2{\cdot}2H_2O$.



$$\underset{\text{(blue, } ex.\ CuCO_3)}{Cu[NH_2SO_3]_2{\cdot}2H_2O} \xrightarrow{\Delta,180} \underset{\text{(Emerald green)}}{Cu[NH_2SO_3]_2{\cdot}H_2O} \xrightarrow{H_2O} \underset{\text{(Emerald green)}}{Cu[NH_2SO_3]_2{\cdot}2H_2O}$$

$$\underset{\text{(blue, } ex.\ Cu[ClO_4]_2)}{Cu[NH_2SO_3]_2{\cdot}2H_2O} \xrightarrow{\Delta,80^\circ} \text{White product} \xrightarrow{H_2O} \text{Blue product}$$

One explanation of this behaviour is that the white product prepared by heating $Cu[NH_2SO_3]_2H_2O$ prepared from $Cu[ClO_4]_2$ is at least partly copper sulphate resulting from the decomposition of the co-ordinated sulphamate group either before or during the heating process. The thermal decomposition of sulphamate ion to sulphate occurs at too high a temperature to be a likely pathway for sulphate formation in the present case, as is demonstrated by the fact that the other form of copper sulphamate is stable at a much higher temperature.

TABLE 2

Electronic spectra and room-temperature magnetic moments *

	Electronic spectra (kK)	μ/B.M.
$[Ni(en)_3][NH_2SO_3]_2$	29.9m; 18.6m; 11.0m	2.96
$[Ni(en)_2(NH_2SO_2)_2]$	27.0m; 16.3m; 10.4, 8.6 (m)	
$[Ni(pn)_2(NH_2SO_3)_2]$	18.3m; 14.4m; 9.6m	2.80
$[Ni(mepn)_2(NH_2SO_3)_2]$	23.0br	Diamagnetic
$[Ni(py)_4(NH_2SO_3)_2]$	See Table 4	3.30
$[Co(py)_4(NH_2SO_3)_2]$	$\overbrace{20.8, 20.0}$s; $\overbrace{9.3, 8.0}$m	5.10
$[Cu(py)_4(NH_2SO_3)_2]$	15.7br	1.96
$[Cu(en)_2(NH_2SO_3)_2]$	13.3br	1.68
$[Cu(en)_2(NH_2CH_2SO_3)_2]$	15.0br	2.00
$Ni[NH_2SO_3]_2{\cdot}4H_2O$	26.0m; 15.4m; 9.2m	3.25
$Ni[NH_2SO_3]_2{\cdot}2H_2O$	23.0m; 12.8m; $\overbrace{7.7m, 6.9}$ (m)	3.20
$Co[NH_2SO_3]_2{\cdot}4H_2O$	21.0, 20.0 (s); 16.4w, sh; 8.4m	5.03
$Co[NH_2SO_3]_2{\cdot}2H_2O$	18.5, 18.0 (s), 16.8sh; 11.4m; $\overbrace{6,87, 6.45}$m	5.27
$Cr[NH_2SO_3]_3{\cdot}4H_2O$	22.8m; 16.5m	5.00
$Cu[NH_2SO_3]_2{\cdot}2H_2O$ (blue) †	14.8br	1.91
$Cu[NH_2SO_3]_2{\cdot}H_2O$ (green) †	13.2br	1.90

* Measurements on complexes of metal sulphamates were carried out on samples that were thoroughly dehydrated, and showed no OH bands in the i.r. region. † Ex $CuCO_3$.

We have repeated these two preparations many times and have confirmed the two types of behaviour. Some preparations of $Cu[NH_2SO_3]_2{\cdot}2H_2O$ from $Cu[ClO_4]_2$ gave a very pale green product on heating rather than a white one, suggesting that a mixture of the two possible products is present. The results for nitrogen analysis of the white (or pale green) product and the blue product formed on hydration varied considerably from sample to sample in some cases none being found. This situation was true to a lesser extent of the original blue product, $Cu[NH_2SO_3]_2{\cdot}2H_2O$; indeed in this case the presence of copper sulphate was confirmed by the comparison of appropriate *X*-ray powder photographs. Copper sulphate was not found in the copper sulphamate prepared from copper carbonate. It was noted, however, that the emerald-green product obtained on heating this form of copper sulphamate showed white patches on long standing (over one year) which were copper sulphate. It appears therefore that decomposition to sulphate also takes place in this case, but more slowly.

We have also prepared $[Zn(H_2O)_4(NH_2SO_3)_2]$ and the anhydrous form, green $Cr[NH_2SO_3]_3{\cdot}4H_2O$, and various Group I and II sulphamates. The Cr^{III} sulphamate lost one mole of water on careful heating. We only observed two absorptions in the spectrum of this compound [$^4A_{2g} \longrightarrow {}^4T_{2g}$ at 16.5 kK, and $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ at 22.8 kK], as the third band expected for O_h symmetry would occur at about 36 kK, outside the range of the instrument we used.

Infrared Spectra.—These are given in Table 3, and allow us to identify the co-ordination mode of the sulphamate ion with some certainty. Our assignments for NH_2 and SO_3 vibrations follow those in the literature [12,13] for sulphamic acid and Group I and II sulphamates. We have confirmed our NH assignments by deuteriation of certain examples.

Three lines of evidence were followed from the i.r. spectra in an attempt to study the co-ordination mode of the sulphamate ion.

(a) *Shifts of* N–H *bands*. This should show the presence of co-ordination of the amino-group, although a possible complication arises from hydrogen bonding effects, as discussed later. In Na^+, K^+, and Ba^{2+} sulphamates, where the sulphamate group is ionic, ν_{NH}(as/s) occur at *ca.* 3 350 and 3 270 cm^{-1}, δ_{NH} at *ca.* 1 550 cm^{-1} (the other δ_{NH} band is masked), NH_2 rock at 900 cm^{-1}. In silver sulphamate, where the silver will be two-co-ordinate, the presence of NH_2 co-ordination is shown by shifts of the N–H absorptions to 3 150, 1 435, and 690 cm^{-1}.

(b) *The* ν_{N-S} *mode*. In the ionic sulphamates this

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[12] A. M. Vaugnat and B. L. Wagner, *J. Chem. Phys.*, 1957, **26**, 77.

[13] L. Kaityar, *Indian J. Pure Appl. Phys.*, 1968, **6**, 686.

mode occurs at *ca.* 800 cm^{-1}. In general it is sensitive to NH$_2$ co-ordination, the frequency dropping *ca.* 50—100 cm^{-1}.

(c) SO$_3$ *Modes.* In theory the presence of oxygen co-ordination of the sulphamate group should be detected by i.r. spectroscopy, in particular by broadening and splitting of the bands at *ca.* 1 100 cm^{-1} as the symmetry of the $NH_2SO_3^-$ group is lowered to C_{2v}. In contrast, amino-co-ordination should not affect the symmetry of the group. However, the study of the SO$_3$ modes proved unhelpful. There are substantial differences in the spectra of the ionic sulphamates in the SO$_3$ region, probably as a result of crystal effects, which suggest caution in the interpretation of these bands. In practice considerable broadening of the SO$_3$ bands takes place in compounds where NH$_2$-co-ordination is postulated. However, it is known that a similar broadening of SO$_3$ modes results from the effect of sulphur co-ordination of the thiosulphate group in metal–thiosulphate complexes.

TABLE 3

Infrared spectra (N–H and N–S regions, in cm^{-1})

	ν_{NH} (as/s)	δ_{NH_2} (as)	δ_{NH_2} (s)	NH$_2$ rock	ν_{NS}
$[NH_3][SO_3]$	3 200s; 3 140s	1 570, 1 530m	1 446m	1 015m	695s
$K[NH_2SO_3]$	3 322s; 3 277s	1 547m	1 125m	957m	790s
$Na[NH_2SO_3]$	3 280m; 3 200br	1 550m	1 125m	915m	800s
$Ba[NH_2SO_3]_2$	3 340s; 3 268s	1 545s	1 155s	915m	760m
$Ag[NH_2SO_3]$	3 150s	1 435m	1 145m	690m	780m
$Zn[NH_2SO_3]_2\cdot 4H_2O$	3 300s; 3 230s	1 552m	1 115m	895m	770s
$Zn[NH_2SO_3]_2$	3 200br	1 430m	1 130w	620s	750s
$Co[NH_2SO_3]_2\cdot 4H_2O$	3 320s; 3 200s	1 530m	1 130m	950s	795s
$Co[NH_2SO_3]_2\cdot 2H_2O$	3 270s; 3 120s	1 440m	1 130m	650m	724m
$Ni[NH_2SO_3]_2\cdot 4H_2O$	Broad band	1 555s	1 100m	960 (sh)	770s
$Ni[NH_2SO_3]_2\cdot 4D_2O$ *	2 380s; 2 250sh	1 150s	975s, sp	625s	765s
$Ni[NH_2SO_3]_2\cdot 2H_2O$	3 230sh; 3 150s	1 440s	1 140m	650sh	775s
$Ni[NH_2SO_3]_2\cdot 2D_2O$ *	2 350s; 2 70sh	1 260m	975s	525sh	785m
$Cr[NH_2SO_3]_3\cdot 4H_2O$	3 150s, br	1 400m	1 145m	615s	720m
$Cu[NH_2SO_3]_2\cdot 2H_2O$ † (blue)	Very broad	1 540m	1 140m	870sh	760m
$Cu[NH_2SO_3]_2\cdot H_2O$ † (green)	3 200s; 3 130sh	1 420s	1 150m	670m	760m
$Cu[NH_2SO_3]_2\cdot 3H_2O$ ‡ (blue)	3 250br	1 415m		620s	
$[Ni(py)_4(NH_2SO_3)_2]$	3 320s; 3 250s	1 565s		870m	788m
$[Cu(py)_4(NH_2SO_3)_2]$	3 230s; 3 120s	Masked		615m	
$[Co(py)_4(NH_2SO_3)_2]$	3 310s; 3 240s	1 575m		870m	790m
$[Zn(py)_4(NH_2SO_3)_2]$	3 370s; 3 250s	1 555m		878m	795m
$[Ni(en)_2(NH_2SO_3)_2]\cdot H_2O$	§	1 555s		878m	798s
$[Cu(en_2)(NH_2SO_3)_2]$	>3 200	1 558s			790s
$[Zn(en)_2(NH_2SO_3)_2]$	§	1 555sh			795s

* Deuteriated. † *ex*-CuCO$_3$. ‡ *ex*-Cu[ClO$_4$]$_2$. § Masked by en absorptions.

$[Zn(py)_4(NH_2SO_3)_2]$ had a poor analysis, and so is not included in the discussion. It is O-bonded. Spectra of $Cu[NH_2SO_3]_2\cdot 2H_2O$ (*ex.* Cu[ClO$_4$]$_2$) and $Cr[NH_2SO_3]_3\cdot 3H_2O$ have similar sulphamate bands to $Cu[NH_2SO_3]_2\cdot 3H_2O$ (*ex* Cu[ClO$_4$]$_2$) and $Cr[NH_2SO_3]_3\cdot 4H_2O$ and so are not listed separately.

The i.r. spectra of $[M(H_2O)_4(NH_2SO_3)_2]$ (M = Co, Ni, or Zn) show that the sulphamate ion is not NH$_2$-bonded to the metal, contrary to expectation. Thus the ν_{NH} frequencies lie in the range 3 320—3 200, δ_{NH} at 1 550, and the NH$_2$ rock mode at *ca.* 900 cm^{-1}. In these cases there is clearly no hydrogen bonding problem, since the NH frequencies are not shifted. On the loss of water molecules (two or four), these absorptions drop in frequency to 3 320—3 150, 1 430, and 650 cm^{-1}, respectively, showing that the NH$_2$ group is now co-ordinated, the sulphamate ion acting as a chelating or bridging ligand. For species $[M(NH_2SO_3)_2]$, hydrogen bonding with aqua-groups is not possible, and it appears unlikely for $[M(H_2O)_2(NH_2SO_3)_2]$. The compound $[Cr(H_2O)_3(NH_2SO_3)_3]$ differs from the $[M(H_2O)_4(NH_2SO_3)_2]$ species in that the i.r. spectra suggests NH$_2$-co-ordinated sulphamate. In this example the possibility of ν_{NH} frequency shifts *via* hydrogen bonding must be considered, although again we do not consider this to be the correct explanation.

Of particular interest are the two forms of copper sulphamate. The product obtained from CuCO$_3$ does not involve NH$_2$-bonded sulphamate, but the green form prepared by heating does; this behaviour is similar to that found for the analogous Co, Ni, and Zn compounds. However, $Cu[NH_2SO_3]_2\cdot 2H_2O$ obtained from Cu[ClO$_4$]$_2$ (which is converted into a white product) clearly does involve NH$_2$-co-ordination. These two forms of $Cu[NH_2SO_3]_2\cdot 2H_2O$ therefore appear to be linkage isomers. The i.r. spectra of the white (or pale green product) were not reproducible from sample to sample, particularly in the 1 200—1 000 cm^{-1} region. We have observed a change in i.r. spectrum with time in certain cases, with the appearance of a strong absorption at 1 100 cm^{-1}, confirming the production of sulphate at room temperature in the mull. It appears therefore that some conversion of the amino-linked copper sulphamate to sulphate takes place during the crystallisation stages, and that this was not necessarily completed after the heating process, so explaining the variable analytical and spectral results obtained. The infrared spectrum for N-bonded blue $Cu[NH_2SO_3]_2\cdot 3H_2O$ is for a sample with correct analysis for nitrogen. The pale green product produced on occasion on the decomposition of N-bonded

$Cu[NH_2SO_3]_2{\cdot}H_2O$ could also arise from the production of a chelating or bridging group, similar to that obtained by heating the O-bonded isomer, the amount of this product reflecting the extent of conversion of the N-bonded isomer to sulphate prior to heating.

Complexes of Metal Sulphamates.—A comparison of complexes of metal sulphamates with well-known ligands with similar complexes of metal halides should be useful in characterising sulphamate as a ligand. I.r., *d–d* spectra, and magnetic moments are in Table 2.

The electronic spectra of $[Ni(en)_2(NH_2SO_3)_2]$ and $[Ni(pn)_2(NH_2SO_3)_2]$ may be assigned in O_h symmetry although there is some splitting of the lowest energy band in the spectrum of the former compound; the magnetic moments are in accord with this. The yellow complex $[Ni(mepn)_2][NH_2SO_3]_2{\cdot}H_2O$ is diamagnetic with an electronic spectrum characteristic of a square-planar complex. It is a 2 : 1 electrolyte in dimethylformamide solution. The complex $[Ni(py)_4(NH_2SO_3)_2]{\cdot}2H_2O$ has non-co-ordinated water, and the electronic spectrum is unaffected by their loss. It is a non-electrolyte in dimethylformamide solution. The two lower energy bands in the *d–d* spectrum are split strongly and may be assigned in D_{4h} symmetry, following Drago.[14] The spectrum was recorded at 77 K and values for parameters obtained by a spectrum fitting procedure.[6] The calculated spectrum with relevant parameters is given in Table 4. Attempts to fit the spectrum to other assignments were unsuccessful. These results allow us to compare $[Ni(py)_4(NH_2SO_3)_2]$ with a range of $[Ni(py)_4X_2]$ complexes, and to compare parameter values for sulphamate ion with those for other axial ligands. This shows for example that Dq for sulphamate is lower than that for Cl^-, suggesting that sulphamate is oxygen co-ordinated in this example.

TABLE 4

Electronic spectrum (cm^{-1}) and parameter values for $[Ni(py)_4(NH_2SO_3)_2]$

Observed	Calculated	Assignment
8 970	8 970	$^3B_{1g} \longrightarrow {}^3E_g[^3T_{2g}(F)]$
12 290	12 290	$\longrightarrow {}^3B_{2g}[^3T_{2g}(F)]$
	12 510	$\longrightarrow {}^1A_{1g}[^1E(D)]$
13 810	13 820	$\longrightarrow {}^1B_{2g}[^1E(D)]$
15 380	15 370	$\longrightarrow {}^3A_{2g}[^3T_{1g}(F)]$
17 420	17 410	$\longrightarrow {}^3E_g[^2T_{1g}(F)]$
22 030	22 350	
23 200	24 090	
	25 600	
	26 960	$\longrightarrow {}^3A_{2g}[^3T_{1g}(P)]$
28 040	28 080	$\longrightarrow {}^3E_g[^3T_{1g}(P)]$

Parameters: $B = 895$, $C = 3\,550$, $Dq = 1\,229$, $Ds = 565$, $Dt = 347$, $Dq_{xy} = 1\,229$; $Cp_{xy} = 1\,570$; $(Cp/Dq)_{xy} = 1.28$; $Dq_z = 620$; $Cp_z = 1\,005$; $(Cp/Dq)_z = 1.62$; $e'_{\sigma xy} = 4\,896$; $e'_{\pi xy} = 599$; $e'_{\sigma z} = 2\,896$; $e'_{\pi z} = 622$.

Hitchman[15] has calculated the angular overlap parameters for the pyridine nickel halide complexes. If his value for the ratio for pyridine is assumed to remain roughly constant throughout the series, then it is possible to calculate the angular overlap parameters for the sulphamate complex. The significant feature is that e'_π for sulphamate is actually larger than e'_π for pyridine, indicating strong π-donation. This is not possible if sulphamate is NH_2-co-ordinated and so again O-co-ordination is indicated. It should be remembered that while the calculation of the angular overlap parameters has involved a considerable number of assumptions and the absolute values may be in error, the general trends in the series should be reasonably accurate so that the conclusion regarding oxygen co-ordination is probably correct.

The complex $[Ni(py)_4(NH_2SO_3)_2]$ lost 3 mol equiv. of pyridine on heating (calculated weight loss 48.1%, found 47.7%), giving bright green $[Ni(py)(NH_2SO_3)_2]$. A similar 1 : 1 complex was obtained on heating $[Co(py)_4(NH_2SO_3)_2]$ (weight loss 41.2% expected 41.7%). A polymeric structure seems most reasonable. A number of $[Co(py)_4X_2]$ complexes are known[16] but a similar comparison of D_{4h} species is not possible, however, since there are still problems in the interpretation of their spectra. The existence of D_{4h} symmetry for $[Co(py)_4(NH_2SO_3)_2]$ is confirmed by the fairly large splitting (1 300 cm^{-1}) of the band due to $4T_{1g}(F) \longrightarrow {}^4T_{2g}(F)$ in O_h symmetry, and by the splitting of the $^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$ band.

The complex $[Cu(py)_4(NH_2SO_3)_2]$ shows one broad band at 15.7 kK, and a normal magnetic moment. $[Cu(en)_2(NH_2SO_3)_2]$ has a low room-temperature moment but measurement of susceptibility down to —140 °C showed no signs of antiferromagnetic interaction. The corresponding species $[Cu(en)_2(NH_2CH_2SO_3)_2]$ had a normal moment and showed one broad band in the visible region, at higher energy than that of the sulphamate.

The i.r. spectra (Table 3) confirm and extend conclusions regarding the co-ordination of the sulphamate group. $[Ni(py)_4(NH_2SO_3)_2]$ shows bands at 3 350, 3 250 (ν_{NH}), 870 (NH_2 rock), and 788 cm^{-1} (ν_{N-S}), all clearly indicative of O-co-ordination in agreement with the conclusions reached from the electronic spectra. The complex $[Co(py)_4(NH_2SO_3)_2]$ is similarly O-bonded, while $[Cu(py)_4(NH_2SO_3)_2]$ involved N-bonded sulphamate. The spectra of the bis(ethylenediamine) complexes are not so straightforward due to the presence of ethylenediamine absorptions, but appear to involve O-co-ordination, as is shown by the data in Table 3.

Conclusions.—It is clear that in the compounds here considered the usual form of co-ordination of the sulphamate ion, when unidentate, is through an oxygen donor atom rather than the NH_2 group, despite the evidence for NH_2-bonding in the complexes reported previously. The existence of sulphamic acid as the zwitterion $NH_3{}^+SO_3{}^-$ emphasises the greater basicity of the nitrogen function and the rather surprising nature of the present conclusion. Only when chelation or bridging is involved do we see NH_2 co-ordination, except in the cases of Cr^{III} and Cu^{II} where there are some

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[14] D. Rowley and R. S. Drago, *Inorg. Chem.*, 1968, **7**, 795.

[15] M. A. Hitchman, *Inorg. Chem.*, 1972, **11**, 2387.

[16] For example, D. W. Herlocker and M. R. Rosenthal, *Inorg. Chim. Acta*, 1970, **4**, 501; B. J. A. Kakazal and G. A. Melson, *ibid.*, p. 360.

examples of simple amino-co-ordination. It is noteworthy that these were the only two metals for which derivatives of $NH_2CH_2SO_3H$ could be prepared.

The existence of ambidentate behaviour and probably linkage isomerism in Cu^{II} sulphamates is of interest in view of the previous suggestion that this occurs for Co^{III} in solution, but it is probably premature to speculate on the pathways to each isomer at this stage, although it should be noted that the acidities of the two preparations are very different. We are studying further the ready conversion of the N-bonded sulphamate species into sulphate, and the slower conversion of the chelated or bridged sulphamates. It should be noted that recrystallisation of the blue N-bonded copper(II) sulphamate led, on one occasion, to complete conversion into sulphate. It is known [1] that refluxing $K_3[Ru(NH_2SO_3)Cl_5]$ (N-bonded sulphamate) in aqueous solution leads to the formation of a nitride species $K_3[RuNCl_8(H_2O)_2]$ and sulphite ion, although the corresponding reaction does not occur for rhodium or iridium analogues. Studies [17] on the hydrolysis of sulphamate ion in perchloric acid at 95 °C show that the reactive species is sulphamic acid, present in solution as the zwitterion. The reactivity towards hydrolysis of the acid is in accord with structure studies which show that S–N bond in sulphamic acid is longer than the one in the sulphamate ion (1.73 and 1.60 Å respectively [18]). It is reasonable therefore that it is the N-bonded copper(II) sulphamate linkage isomer that undergoes decomposition to the sulphate, resulting from a weakening of the N–S bond through co-ordination and possibly the ready availability of a co-ordinated water molecule for a subsequent hydrolysis reaction, generating ammonia and sulphate ions. The ammonia molecules may remain co-ordinated to the copper, accounting for the presence of nitrogen in the analysis of compounds which had apparently been converted into sulphates, and weak absorptions at 1 595 cm^{-1} in their i.r. spectra. The lack of reactivity of the O-bonded linkage isomer is in accord with the i.r. evidence which shows that ν_{N-S} modes in general do not shift on oxygen co-ordination of sulphamate.

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[18] F. A. Kanda and A. J. King, *J. Amer. Chem. Soc.*, 1951, **73**, 2315; G. A. Jeffrey and H. P. Stadler, *J. Chem. Soc.*, 1951, 1467.