Chem. Soc. Rev., 1988, **17**, 181—227

The Chemistry of Molten Acetamide and Acetamide Complexes

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1 Introduction

Molten acetamide is a currently under-appreciated non-aqueous liquid with unusual and useful properties. Its melting point, stability, and cost make it convenient to use and its dipolar nature makes it a particularly good solvent; unusually it is equally good for both ionic inorganic and for covalent organic compounds. Stafford[1] reported more than 50 years ago that over 400 organic compounds dissolved in molten acetamide and over 200 inorganic compounds. In fact the only substance found to be insoluble was cellulose. Unfortunately no solubility values were quoted in this report, but more recently 65 solubilities have been determined, all substantial.[2]

The earlier review[3] (following up an extensive paper[4]) noted the 'water-like' properties of molten acetamide in physical properties, acid–base reactions and in coordination, but concentrated largely on the first. The only other general review[5] published in 1967, apart from a more recent but inaccessible work in Russian,[6] was a somewhat short summary of the known information, though more specialized accounts, for example of acid–base interactions,[7] have been published.

This review endeavours to deal comprehensively with the now very extensive published work on the chemistry of molten acetamide and includes consideration of acetamide complexes with metals and non-metals since there is an obvious relationship between such complexes and the interactions of the appropriate ions in molten acetamide solution. Thus data on the stoicheiometry and significant properties of the former (*e.g.* mode of bonding, thermal stability) have been included even when such complexes have been prepared from acetamide dissolved in another solvent (often water, alcohols, ethers, benzene, or carbon tetrachloride) rather than from molten acetamide. However, the quite extensive chemistry of acetamide dissolved in such solvents will not otherwise be considered.

The other boundaries of this review are that the purely organic reactions of acetamide will not be dealt with, nor in general will the chemistry of formamide, the

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[1] O. F. Stafford, *J. Am. Chem. Soc.*, 1933, **55**, 3987.

[2] R. C. Paul and R. Dev, *Res. Bull. Panjab Univ., Sci.*, 1969, **20**, 139.

[3] G. Winkler, 'Chemie Nichtwässerungen Ionisierenden Lösungsmitteln', ed. G. Jander, H. Spandau, and C. A. Addison, Interscience, 1963, Vol. 4, 203.

[4] G. Lander and G. Winkler, *J. Inorg. Chem.*, 1959, **9**, 24.

[5] J. W. Vaughn, 'The Chemistry of Non-Aqueous Solvents', Vol. II, ed. J. J. Lagowksi, Academic Press, New York, 1967.

[6] B. Imanakunov, Vzaimodeistvie Atsetamida s Neorganicheskhimi Solyami, Ilim: Frunze, Kirg SSR, 1976.

[7] S. Guiot and B. Tremillon, *J. Electroanal. Chem.*, 1968, **18**, 261.

higher homologues or the alkyl-substituted derivatives of acetamide be considered.

2 Properties of Pure Acetamide

A. Crystal Structure.—Solid acetamide is known in two crystal forms. The stable modification is trigonal (rhombohedral)[8] and is obtained by crystallization of solutions in organic solvents (*e.g.* ethyl acetate) and has a melting point usually quoted as 81 °C, but recently also as 82[9] and 80.3 °C.[10] The acetamide molecules have been shown to be in the keto form with the amino group in the plane of the carbons, bond distances agreeing both from *X*-ray diffraction[8] and from neutron diffraction[11] measurements. There are numerous hydrogen bonds to three other molecules.

The metastable orthorhombic crystal form is obtained by crystallization of molten acetamide,[12,13] (though rhombohedral crystals grown from the melt have also been claimed[14]) with a lower melting point: values of 69—73 °C have been quoted. The bond distances are similar to those in the stable form, the differences lying in the many hydrogen bonds which initially result in dimers that are further linked together in columns.

B. Preparation and Purification.—Acetamide is prepared by many reactions,[15] including

$$\left.\begin{array}{l}\mathrm{MeCO_2Et + `(NH_4)_2CO_3'}\\ \mathrm{MeCO_2Et + NH_3}\\ \mathrm{MeCOCl + NH_3}\\ \mathrm{(MeCO)_2O + NH_3}\end{array}\right\}\longrightarrow \mathrm{NH_4OOCMe}\xrightarrow{\Delta}\mathrm{MeCONH_2 + H_2O}\qquad\begin{array}{r}(1)\\(2)\\(3)\\(4)\end{array}$$

$$\mathrm{MeCN + H_2O \longrightarrow MeCONH_2} \tag{5}$$

$$\mathrm{CH_2{=}C{=}O + NH_3 \longrightarrow MeCONH_2} \tag{6}$$

but the most efficient commercially involve distillation of ammonium acetate at 100—200 °C to give a 95% pure product from which the reagent grade is obtained by recrystallization (product >99%, 0.25% H_2O, melting point 79—81 °C). The technical grade contains ~0.75% water, with melting point 78—82 °C. Acetamide is odourless if pure, the mouse-like smell arising from an unidentified impurity.

Since acetamide is hygroscopic, several methods for removal of water have been

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[8] F. Senti and D. Harker, *J. Am. Chem. Soc.*, 1940, **62**, 2008.

[9] L. Vogel and H. Schubert, *Wiss. Z. Martin-Luther-Univ.*, 1985, **34**, 79.

[10] H. G. M. De Wit, C. G. De Krnif, and J. C. Van Miltenburg, *J. Chem. Thermodyn.*, 1983, **15**, 891.

[11] G. A. Jeffrey, J. R. Ruble, R. K. McMullan, D. J. De Frees, J. I. Binkley, and J. A. Pople, *Acta Crystallogr., Sect. B*, 1980, **36**, 2292.

[12] W. C. Hamilton, *Acta Crystallogr.*, 1965, **18**, 866.

[13] W. A. Denne and R. W. H. Small, *Acta Crystallogr., Sect. B*, 1971, **27**, 1094.

[14] T. Ottersen, J. Almlof, and H. Hope, *Acta Crystallogr., Sect. B*, 1980, **36**, 1147.

[15] 'Kirk-Othner Encyclopaedia of Chemical Technology', 3rd Edn., J. Wiley, 1978.

proposed. On a laboratory scale a much used method for removal of most water is distillation, with rejection of the fraction boiling below 210 °C. However a drawback is that small quantities of acetonitrile are formed by dehydration[16] (*i.e.* reverse of equation 5). The recommended method is therefore to dissolve reagent grade material in hot dry methanol (saturation is ~ 125 g per 100 ml) and then treat the cooled solution with an excess of dry diethyl ether (~ 8 ml per g acetamide). The precipitated solid is filtered and then vacuum dried.

C. Pyrolysis.—Acetamide has a boiling point of 221 °C,[3] but the vapour begins to decompose at relatively low temperatures (at 220 °C forming ~0.1 mole% NH_3, ~0.05 mole% MeCN and $MeCO_2H$)[17] and rate measurements at higher temperatures have shown the process to be second order in acetamide, the suggested reaction being:

$$2MeCONH_2 \longrightarrow MeCO_2H + MeCN + NH_3 \qquad (7)$$

Hydrogen chloride has a marked catalytic effect (× 10 rate) which suggested that conversion of acetamide into the hydroxyimide form was required before a rapid reaction took place.[18,19]

These findings suggest that the preparative reactions (equations 1—5) involve a number of equilibria other than those stated.

D. Toxicity.—Acetamide occurs in small quantities quite widely in nature. For example it has recently been reported as a minor constituent of the aroma of Tilsit cheese,[20] and of the odour of poultry manure.[21] Acetamide has also been widely used for many years in a variety of industries (production was ~230 tons per annum in 1976), including the manufacture of cosmetics, textiles, lacquer, leather, paper, explosives, insecticides, and plastics, principally as a humectant and plasticizer, but also as a peroxide stabilizer and ingredient of soldering fluxes. New uses are also being proposed, for example as a de-icing agent.[22] These widespread albeit relatively small scale uses have indicated that with normal handling and precautions there are no significant hazards to human beings, though it is a mild irritant and has a low toxicity.[15]

Tests on white mice indicated the maximum tolerated dose was 12 g kg^{-1} body weight and that the minimum lethal dose was 15 g kg^{-1}.[23] In addition rats fed on a diet containing 2.5% acetamide for 12 months developed malignant liver tumours (at 36% incidence, but 13% with 5% acetamide)[24] which were consistent with the hypothesis of chronic intracellular liberation of ammonia. No tumours were found

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[16] E. C. Wagner, *J. Chem. Educ.*, 1930, **7**, 1135.

[17] D. Davidson and M. Karten, *J. Am. Chem. Soc.*, 1956, **78**, 1066.

[18] M. Hunt, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1965, 5074.

[19] J. Aspden, A. Maccoll, and R. A. Ross, *Trans. Faraday Soc.*, 1968, **64**, 965.

[20] K. N. Ney, *Feite, Seifen, Anstrichm.*, 1985, **87**, 289.

[21] A. Yasuhara, *J. Chromatogr.*, 1987, **387**, 371.

[22] R. Vogel, West German Patent, DE 3434953, 1986.

[23] F. Bergmann and L. Haskelburg, *J. Am. Chem. Soc.*, 1941, **63**, 1437.

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in other organs.[25] This report resulted in acetamide being placed prominently on lists of carcinogens, despite the relatively massive dose involved. However, more recent studies have shown acetamide to have no mutagenicity towards lower organisms (*Aspergillus nidulans*[26] and *Salmonella typhimurium*[27]), nor towards *Drosophilia melanogaster.*[28] In additon it did not cause DNA damage to rat hepatoma cells, or to primary Syrian hamster embryo cells. Interestingly, it was found not to damage liver cells *in vivo.*[27]

E. Physical Properties.—Extensive lists of the older values are given in Winkler,[3] but more recently the density of molten acetamide has been given as:

$$\rho/\mathrm{g\,cm^{-3}} = 1.3576 - 0.0012T + 0.64 \times 10^{-6}\,T^2 \qquad (8)$$

together with values for the heat capacities of the solid and the melt.[9]

The latent heat of fusion and the thermal conductivity, both important parameters in the possible use of acetamide as a phase-change thermal energy storage material, have recently been remeasured. The former has been given as 249,[9] 225,[29] 264,[30] 265[10] kJ kg^{-1}, which are not dissimilar to the older value of 252 kJ kg^{-1},[31] though lower than the 278 kJ kg^{-1} determined in 1914[32] and still quoted.[3] Moreover, whatever the precise value proves to be, it is evident that it is satisfactorily high for its intended use, and indeed higher than that for most organics (*e.g.* diphenyl 140, palmitic acid 165 kJ kg^{-1}) and that for a number of inorganic salts (*e.g.* KBr 215, $NaNO_3$ 174 kJ kg^{-1}).[33]

The most recent report gives the thermal conductivity as 0.287 W m^{-1} K^{-1} at 50 °C and 0.240 at 91 °C,[34] which reinforce the single values (0.252 and 0.263) given thirty years before,[35,36] and indicate only a 2% change on melting. The electrical conductivity of the solid is low (*e.g.* 3.0×10^{-8} Ω^{-1} cm^{-1} at 80 °C) and has been attributed to proton transfer,[37] but no corresponding values for the melt appear to have been published.

The dipole moment of acetamide in dioxane and benzene solutions have been measured several times[38–43] and the calculated values of 3.87 and 3.92D

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[27] E. Dybing, W. P. Garden, E. J. Soederlund, J. A. Holme, and E. Rivedal, *Adv. Exp. Med. Biol.*, 1986, 197.

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[43] W. D. Kumler and G. W. Porter, *J. Am. Chem. Soc.*, 1934, **56**, 2549.

respectively at 25 °C are consistent with a planar, keto structure.

Magnetic susceptibilities of -3.50 and -3.32×10^{-10} m^3 mol^{-1} for solid acetamide[44,45] and refractive indices of 1.4890 for the solid and 1.4270 for the melt have been reported.[46]

F. Vibrational Spectroscopy.—The infrared absorption bands of acetamide–metal complexes have been much studied, since certain shifts from the values of acetamide alone have been taken as diagnostic of coordination to metal *via* oxygen or *via* nitrogen. The band positions (and their assignment) that have been quoted for acetamide alone do vary somewhat: a compilation in chronological order is given in Table 1. However these measurements have been made on solid acetamide or its solutions, while molten acetamide has only been the subject of two studies.[47,48] The later and more quantitative[47] showed 17 absorption bands at 95 °C which included those of Table 1 though often with quite different intensities [the relevant frequencies, intensities, and assignments are: 3 343(3.5) and 3 191(3) NH vibrations; 2 997(7) and 2 935(26) C–H vibrations; 1 664(11.5) and 1 612(6.5) C=O vibrations; 1 418(2), 1 388(9.5), and 1 348(8.5) C–H deformations; 1 123(9.5) NH_2 rock; 1 001(2.5), 955(2), and 862(24) chain vibrations; 570(9) and 447(8) CON deformations]. Most interestingly a new line at 984 cm^{-1} appeared in melts at 71 °C and intensified as the temperature was lowered (acetamide can be readily supercooled). This new line was attributed to the β (orthorhombic) crystal form, because of its lower symmetry. Simultaneously with the appearance of the new line, the 570 cm^{-1} band shifted to 593 cm^{-1} and the intensity of the 862 cm^{-1} band fell. The intensities of the 1 664 and 1 612 cm^{-1} vibrations decreased from 90 °C which indicates a progressive change in the proportions of the α and β forms. These changes were not simply the formation of the imidazole form, since they were 'eliminated by monoallylation' (presumably of the amide group) which 'does not prohibit tautomerization'.[47] The earlier brief report, for which no temperature was given for the 'molten acetamide', broadly confirmed the positions of the high temperature bands.[48] The broad 3 172 cm^{-1} band has also been cited as evidence of dimerization[49] and the 3 484—3 513 cm^{-1} band of the formation of di-, tri-, and tetramers in carbon tetrachloride solution.[50] However the shifts in these bands found with lithium chloride and lithium perchlorate solutions have been interpreted in terms of hydrogen bonds to the anions and Fermic resonance, rather than in terms of changes in the association of the solvent molecules.[51]

Part of the difficulty of interpretation of the acetamide infrared spectrum lies in the fact that many absorptions are not localized between particular pairs of atoms.

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Table 1 *Infrared absorption bands of acetamide and their assignments*

Band frequency (cm^{-1}) *and assignment*										*Medium*	*Ref.*
3 359 3 436	N-H	1 685	Amide I	1 595	Amide I					CH$_2$Cl$_2$ solution (dilute)	*a*
3 333 3 175	N-H	1 685	Amide I	1 626	Amide II					Liquid paraffin mull	*a*
3 532(6) 3 412(6) [2 977(8)	N-H C-H]	1 704(9) 1 679(10)		1 595(6)	N-H	1 440 (sh) 1 407 (sh) 1 381(6) 1 339(5)	C-H	119(2)	N-H	CHCl$_3$ solution	*b*
3 477(6) 3 375(6)	N-H	1 709(9) 1 684(10)		1 616(7)	N-H	1 335(7)	C-H	1 122(5)	N-H	MeCN solution	*b*
3 550(8) 3 450(6) 2 967(6) 2 860(6) 1 900(2)	N-H C-H	1 733(10)		1 600(9)	N-H	1 385(8) 1 319(8)	C-H C-H	1 134(5)	N-H	Gas 180 °C	*b*
3 330(10b) 3 160(10b)	N-H	1 681(10) 1 678 (sh) 1 651 (sh)		1 610(9)	N-H	1 458(4) 1 362(6) 1 357(6) 1 399(8)	C-H	1 152(6)	N-H	α-form mull?	*b*
3 330(10) 3 165(10)	N-H	1 660(10)				1 471(7) 1 449(7) 1 359(8) 1 397(10)	C-H	1 152(8) 1 144(4b)	N-H	β-form mull?	*b*

Table 1 (continued)

Band frequency (cm^{-1}) *and assignment*												*Medium*	*Ref.*
3 340 (s) 3 180 (s)	N–H	1 684 (s)	Amide I	1 629 (s)	Amide II	1 410 (m)	C–N	1 140 (s) 1 045 (m)	N–H rock	1 014 (w)	C–H bend	?	*c*
3 545 3 430	N–H	1 675	Amide I	1 595	Amide II	1 385	C–H	1 335	C–N				*d*
3 540	N–H asym											CCl_4 solution	*e*
3 412	N–H sym												
3 365 3 190	N–H	1 670	C=O									CH_2Cl_2 solution	*f*
3 560 (s)	N–H asym	1 710 (s)	Amide I	1 605 (s)	Amide II	1 380 (s)	C–N					$CHCl_3$ solution	*g*
3 440 (s)	N–H sym	1 685 (s)											
3 445	N–H	1 685	C=O			1 410	C–N						*h*
3 440 3 180	N–H	1 684	C=O			1 410	C≡N						*i*
3 440 (3 110)	N–H	1 685	Amide I	1 629	Amide II	1 410	C–N						*j*
3 290	N–H asym			1 640	C–C							Nujol or HFBD mull	*k*
3 138	N–H sym												
3 360	N–H	1 665	C=O	1 620	NH_2 bend	1 395	C–N					?	*l*
		1 695	C–O			1 410	C–N			760	N–C–O bend		*m*

Table 1 (*continued*)

Band frequency (cm^{-1}) *and assignment*										*Medium*	*Ref.*
3 340 (s) 3 160 (s)	N–H	1 680				1 410 (s)					*n*
3 350 (s)	N–H asym	1 665 (s)	C=O			1 405 (m)	C–N			Nujol mull and KBr pellets	*o*
3 180 (s)	N–H sym										
		1 670	C=O			1 390	C–N	1 140	NH_2 rock	CsI discs	*p*
3 290 3 180	'H_2O and NH_3'	1 660	C=O	1 505	C–N	1 395	N–H	1 145	NH_2 rock	Liquid paraffin mull	*q*

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For example while the band labelled 'Amide I' (Table 1) is almost exclusively (>80%) due to the carbonyl stretching mode the amide II band is stated to have contributions both from the NH in-plane bending (~60%) and from CN stretching modes, and the amide III band (position not quoted for acetamide) includes CN stretching (~40%), NH in-plane bending (~30%) and CH deformation modes,[52] these assignments being based on a theoretical treatment of *N*-methyl acetamide.[53] Part of the variation in experimental values for these and other bands (Table 1) is due to changes in intermolecular hydrogen bonding between the solid state and solution which particularly effects the NH and CO absorptions, and even the concentration of the solution introduces considerable variation, dilute solutions showing the least hydrogen bonding.[52]

Such variations naturally complicate comparisons and even assignments, since solution concentration is rarely quoted, and also complicate deductions about the mode of bonding of metal cations. Coordination through oxygen reduces the CO bond order, and hence amide I frequency values of around 1 650—1 660 cm^{-1} are often quoted. The amide II band decreases somewhat (~1 590—1 610 cm^{-1}) and the amide III band shows irregular variation. The N–H stretching frequencies increase from the solid state values, but decrease from those of dilute solution, so that the basis of comparison needs to be clear. The band around 1 400 cm^{-1} variously attributed to CH or CN bonds generally increases (by ~10—20 cm^{-1}) on coordination of oxygen to metal. By contrast bonding of metal cations through nitrogen would be expected to decrease the N–H stretching frequencies still further (due to increased hydrogen bonding) and also increase the frequency of the amide II band. Further changes are not easy to predict, and no stable example is available for study.

In contrast the acetimidate anion ($MeCONH^-$) does bond in metal complexes *via* nitrogen, and is observed to produce a marked lowering of the amide I band (to ~1 550—1 600 cm^{-1}) a further band around 1 480 cm^{-1}, a strong C–H band (~1 420 cm^{-1}) and slightly less strong N–H bands (around 3 250 cm^{-1}).[54]

A few Raman measurements have been reported[54] and some infrared bands of deuterated species (together with cryoscopic and ebullioscopic measurements which showed the presence of dimers and trimers in solution).[55–57]

Proton[58,59] and ^{15}N n.m.r.[60] measurements have been made in various solvents. Protonation of carbonyl oxygen in fluorosulphuric acid was indicated,[61] with just enough protonation of amide nitrogen when in liquid ammonia to explain the con-

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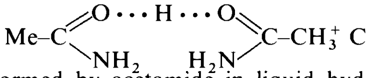
siderable increase in N exchange rate when ammonium chloride was present.[62,63] N.m.r. measurements also indicated a change to acid-catalysed proton exchange, *via* nitrogen-protonated intermediate species, as the solvent polarity was increased (the change over in mechanism occurred with 90% aqueous THF).[64]

3 Reactions of Acetamide

A. Acidic and Basic Reactions.—The 'water-like' nature of molten acetamide has long been known,[4] the auto-dissociation constant being given as 3.2 × 10^{-11} at 94 °C, and thus the possibility of it acting as a medium for acidic and basic

$$2\mathrm{MeCONH_2} \rightleftharpoons [\mathrm{MeCONH_3}]^+ + [\mathrm{MeCONH}]^- \qquad (9)$$

reactions together with the formation of compounds with both acids and bases. A correlation of the pH scale in water with that in acetamide has been made.[7]

Hydrogen chloride was noted as early as 1857 to form a 1:1 compound with acetamide solutions (such compounds can also be called complexes or solvates). This, under vacuum and over sodium hydroxide, lost hydrogen chloride, forming a stable 1:2 compound,[65] the melting point being given as 135 and 131 °C respectively.[48] These compounds were considered to be substituted ammonium and oxonium salts respectively ($\mathrm{MeCONH_3{}^+Cl^-}$ and  $\mathrm{Me{-}C(=O\cdots H\cdots O=)(NH_2)\ (H_2N)C{-}CH_3^+\ Cl^-}$).[66] The former 1:1 compound was also formed by acetamide in liquid hydrogen chloride and was also considered ionic.[67] Structure of the latter 1:2 compound, called the 'hemihydrochloride', has been confirmed as having strong hydrogen bonds, with hydrogen situated between two carbonyl oxygens themselves only 2.451 Å apart,[68] while the intense infrared absorption between 600 and 1 600 $\mathrm{cm^{-1}}$, with a maximum at 800—900 $\mathrm{cm^{-1}}$ [69] that changed little on deuteration (centre of gravity ~920 $\mathrm{cm^{-1}}$)[70] was also taken to indicate a non-centred double minimum bond.[71] Raman absorptions have been reported.[48] 1:2 Acetamide compounds have also been claimed with hydrogen bromide (m.p. 142 °C),[4] and with hydrogen iodide.[72]

With nitric acid, 1:1 and 1:3 compounds were formed whose crystal parameters have been determined (m.p. 99 °C and 71 °C respectively), the bond lengths of the

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[72] G. Winkler, Dissertation, Tech. Univ. Berlin, 1957.

former clearly showing a protonated carbonyl oxygen[73,74] (rather than a protonated amine group). The crystal structure of the latter compound showed short, almost symmetrical, hydrogen bonds between the proton and the oxygens of the two acetamides, the oxygens of the nitrate anion each being coordinated by two amine groups.[75] Infrared and heat of combustion measurements have also been made.[54,75] A 1:2 compound was found[4] with perchloric acid (m.p. 91 °C) but in contrast a 2:1 compound was reported with meta-iodic acid, though a structure was not determined.[73] With trichloroacetic acid both 1:1 and 2:1 compounds were found;[76] solutions of the latter decarboxylated slowly at 100 °C.[77] acetic acid only a 1:1 compound was detected (m.p. < 2.5 °C).[78] Titrations of perchloric acid in molten acetamide with sodium and potassium acetimide have confirmed the 1:2 compound,[79] and the formation constant of this has been determined in acetic acid solution.[80] The relative strength of a number of protonic acids at 100 °C in molten acetamide has been given as $HSO_3F > H_2SO_4 >$ picric acid $> Cl_3CCO_2H >$ salicylic acid $> Cl_2HCCO_2H > ClCH_2CO_2H >$ benzoic acid $> CH_3CO_2H$,[78,81] and as $HClO_4 > HNO_3 > HBr > HCl >$ picric acid $>$ *p*-toluene sulphonic acid.[4] Measurements of specific conductance, density, viscosity, and transference numbers have been made with solutions of sulphuric acid (shown to form 1:1 and 1:2 compounds) and of phosphoric acid (only a 1:1 compound). Labelling these acids (with ^{35}S and ^{32}P, and the acetamide with ^{14}C) has shown a prototropic (or 'proton hopping') mechanism to be occurring at 0.4 to 1.0 mole fraction of acid, and almost zero ionic migration. However, in more dilute solutions (< 0.4 M) labelled carbon migrated to the cathode (as protonated acetamide) and, in the case of sulphuric acid, only labelled sulphur to the anode (as HSO_4^-, which was thus not solvated).[82–84] At higher temperatures with concentrated sulphuric acid, decomposition occurred (46.4% decomposition at 300 °C, forming 0.91 millimoles SO_2, 1.20 CO_2, and 0.29 CO per millimole acetamide).[85] Long chain aliphatic acids (lauric, myristic, palmitic, and stearic acids) form 1:1 complexes.[86]

Ammonia has been stated to be insoluble in molten acetamide at 94 °C,[77] but had earlier been presumed to form a 1:1 compound.[78] However, compounds have not been reported with organic nitrogen bases, though measurements of con-

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[86] F. C. Magne and E. L. Skau, *J. Am. Chem. Soc.*, 1952, **74**, 2628.

ductivity and infrared absorptions have been taken to indicate attachment to acetamide *via* its amine group, or even protonation of the bases,[77,81] similar shifts being observed as for coordination of a Lewis acid to carboxyl oxygen. The alkali metal compounds formed by reacting the metal with acetamide in dry organic solvent (dioxan for sodium, benzene for potassium),[4,87] by distilling ethanol from a solution of acetamide in ethanol containing 5% sodium ethoxide, or by the reaction of sodamide with molten acetamide,[3] are certainly ionic (m.p. of NaNHCOMe 315 °C[48]) and an infrared study has shown the 24 bands to be very similar to those from carboxylates.[54,88,89] Lithium acetimidate has been made by ion exchange of the sodium acetimidate in molten acetamide,[90] and both lithium and sodium compounds by solvolysis of the alkali metal hydrides with the melt.[91] Basic solutions of lithium, sodium, or potassium acetimidates, as well as of organic bases (*e.g.* pyridine, quinoline, benzylamine, and piperidine) have been titrated conductiometrically against solutions of many acids with results in accord with the autodissociation (equation 9 above).[7,77,79,81,82,91,92] Though it was early claimed that the equivalent conductances indicated that all salts [except the zinc, cadmium, and mercury(II) halides] were completely dissociated in molten acetamide,[4] the degree of dissociation has since been shown to be smaller in most cases (varying for example from 96.4% for Et_3NHBr to 64.5% for LiO_2CMe).[93]

B. Main Group Elements.—(i) *Reactions of Alkali Metal Cations.* In this and succeeding sections compounds of acetamide not conveniently listed as acids or bases (in Section 3A) will be considered on the basis of the Periodic Table, even though decisions about the most significant other element present are somewhat subjective.

As would be expected lithium cations were shown by *X*-ray diffraction analysis to be coordinated to, and bridged by, acetamide molecules [*e.g.* in solid $Li(MeCONH_2)_{3/2}(MeCONHCOMe)ClO_4$[94]] and 0.1 M solutions of lithium perchlorate were stable enough at 99 °C to act as the supporting electrolyte in polarographic studies.[95] Lithium nitrate has been claimed to form both a 1:1 and 1:2 complex (m.p. 137 and 105 °C) with two eutectics[96,97] though another later phase diagram study found no compounds and only one eutectic.[98] But both sets of measurements of electrical conductivities, densities, and viscosities (over a composition range from 25 to 225 °C) agree that a break in the property/composition

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[98] I. M. Bokhovkin and E. D. Vitman, *Zh. Obshch. Khim.*, 1965, **35**, 949.

curves occurs at the (lower) eutectic, as is found in hydrate systems.[96,97,99] The phase diagrams, densities, viscosities, and electrical conductivities of lithium, sodium, potassium, and ammonium nitrates with acetamide have also been reported,[98,100,101] together with electrochemical measurements.[92] This considerable amount of activity arises from the possible applications of lithium nitrate batteries, where even small amounts of acetamide increase anodic current densities significantly and hence the utilization of metallic lithium.[102]

The solubilities of five sodium and potassium halides in molten acetamide have been reported.[103–107] Best values have been given.[108] Phase diagram and refractive index measurements on the aqueous acetamide lithium chloride system have indicated two compounds ($LiCl{\cdot}2MeCONH_2{\cdot}H_2O$ m.p. 48—50 °C and $LiCl{\cdot}MeCONH_2{\cdot}H_2O$ 'melting over a broad range').[109] Phase diagram[110–112] and crystallographic[113,114] studies have also indicated the formation of other compounds ($NaBr{\cdot}2MeCONH_2$, $NaI{\cdot}2MeCONH_2$ and $KI{\cdot}6MeCONH_2$ melting points 144, 110, and 55 °C respectively) and their Raman absorptions have been reported.[48] The ionic nature of acetamide solutions of alkali metal halides and pseudo-halides has been shown by their high conductivities[104,111,115] and solubility decreases with addition of a common ion.[104] Viscosities,[116] densities,[117,118] and enthalpies of solutions[119–121] have been measured over a range of concentrations and of temperatures (85—115 °C) and indicate an increasing disruption of the spacial network of hydrogen bonds by the added ions as the temperature increased. Similar conclusions arose from paramagnetism measurements.[122] This ionic nature has also allowed successful quantitative polarographic determination of potassium in a number of complexes,[95] and the successful ion exchange of all the

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[100] D. A. Tkalenko, S. A. Kudrya, A. A. Rudnitskaya, and N. A. Chmilenko, *Fiz. Khim. Svoistva Rasplovl Tverd. Elektrolitov*, ed. Y. K. Delimarskii, 1979, 66.

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[121] S. Taniewska-Osinka and M. Woldan, *Zh. Fiz. Khim.*, 1974, **48**, 2154.

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alkali metal cations (as chlorides) in molten acetamide on powdered zirconium phosphate.[123]

(ii) *Alkaline Earth Metal Cations.* Much information on the interactions of alkaline earth cations with acetamide has been obtained from aqueous solutions, mainly by phase diagram investigations[124–130] but also from density,[131] viscosity,[131] electrical conductivity,[131] DTA,[132] and TG[133,134] measurements (alkaline earth metal oxide being the final product). Naturally the compounds claimed have usually been acetamide hydrate complexes as well as anhydrous (the stoicheiometries being listed in Table 2) with the proportion of acetamide in the complex increasing with the concentration of acetamide in the aqueous solution. Infrared spectroscopy indicated coordination of acetamide through oxygen.[132,134] Interfacial tension measurements between aqueous acetamide solutions and immiscible organic liquids (isoamyl acetate, n-hexyl alcohol) have also been claimed to show association,[135] (the stoicheiometries being $MCl_2{\cdot}2MeCONH_2$, $MCl_2{\cdot}MeCONH_2$, $2MCl_2{\cdot}MeCONH_2$ in the case of $SnCl_2$ and $BaCl_2$, but only the first two with $MgCl_2$).

Table 2 indicates that there is no overall trend in melting or decomposition temperatures with varying ratios of acetamide, or of acetamide/water, nor any apparently preferred coordination number though structure determination may reduce the ostensible spread of 3 to 7.

Interestingly, problems attributed by the authors to hydrolysis were reported in establishing the composition of the solid phase formed with magnesium chromate and certainly magnesium hydroxide was precipitated.[122] However in view of the reactivity of chromium(VI) with acetamide melts (Section 3C, iv) it seems possible that the problems were due to some reduction to chromium(III) with resulting increase in the basicity of the solution and consequent precipitation of magnesium hydroxide.

Solutions of alkaline earth halides and of alkali metal halides have been the subject of extensive physical measurements, including densities,[117] viscosities,[116] enthalpies,[119–121] Raman and infrared spectroscopy,[48] electrical conductivities,[115] and potentiometric titrations.[136]

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Reactions have also been reported, calcium hydride solvolysing[91] and calcium metal reacting vigorously and forming hydrogen in molten acetamide.[107]

Table 2 *Complexes of acetamide with alkaline earth metal salts (stoicheiometries, densities, melting points, and decomposition temperatures)*

Stoicheiometry	*Colour*	*Density*	*Melting Point* (°C)	*Decomposition Temperature* (°C)	*Ref.*
$BeCl_2 \cdot MeCONH_2 \cdot 3H_2O$		1.2712		311	*a b*
$BeCl_2 \cdot 3MeCONH_2 \cdot 2H_2O$		1.2224		380	*a, b*
$BeSO_4 \cdot 2MeCONH_2 \cdot H_2O$		1.4460	136	231	*a, c*
$MgCl_2 \cdot 2MeCONH_2$	white		68		*d*
$MgCl_2 \cdot 4MeCONH_2$			153		*e*
$MgCl_2 \cdot 4MeCONH_2 \cdot 2H_2O$		1.3790	150—3	290	*a, b, f*
$MgBr_2 \cdot 6MeCONH_2$			169, 170		*e, g*
$MgI_2 \cdot 6MeCONH_2$			177		*g*
$Mg(SCN)_2 \cdot 4MeCONH_2$					*h*
$Mg(ClO_4)_2 \cdot 5MeCONH_2$					*i*
$Mg(ClO_4)_2 \cdot 7MeCONH_2$					*i*
$Mg(NO_3)_2 \cdot 4MeCONH_2 \cdot H_2O$			60—5		*j, k*
$Mg(NO_3)_2 \cdot 4MeCONH_2 \cdot 2H_2O$			45	390	n, *o*
$Mg(NO_3)_2 \cdot 6MeCONH_2 \cdot 2H_2O$			110	410	*n, o*
$Mg(O_2CMe)_2 \cdot 2MeCONH_2$					*p*
$MgSO_4$—no compound					*a*
$MgCrO_4 \cdot MeCONH_2 \cdot 6H_2O$					*l*
$CaCl_2 \cdot MeCONH_2$					*m*
$CaCl_2 \cdot 3MeCONH_2$				186	*m*
$CaCl_2 \cdot 4MeCONH_2$	white		72, >240	>240	*d, q, r*
$CaCl_2 \cdot 6MeCONH_2$			62, 64		*g, m*
$CaCl_2 \cdot 2MeCONH_2 \cdot 2H_2O$					*b*
$CaCl_2 \cdot 4MeCONH_2 \cdot 2H_2O$					*b*
$Ca(O_2CMe)_2$—no compound					*s*
$CaSO_4$—no compound					*a*
$SrCl_2$—no compound					*a*
$SrSO_4$—no compound					*a*
$BaCl_2 \cdot 6MeCONH_2$	white		60		*d*
$BaCl_2$—no compound					*a*
$BaSO_4$—no compound					*a*

[a] S. Baichalova and B. Imanakunov, *Izv. Akad. Nauk Kirg. SSR*, 1968, 64. [b] B. Imanakunov, S. Baichalova, P. Yun, and A. Dzhunusov, *Mater. Nauchno-Tekh. Konf. Posuyshch. 100(Sto) Letiyu Period Zakona D. J. Mendeleeva*, 1969, 85. [c] E. A. Gyunner, *Zh. Neorg. Khim.*, 1962, **7**, 1431. [d] R. C. Paul and R. Dev, *Indian J. Chem.*, 1967, **5**, 267. [e] L. Kahovec and K. Knollmullor, *Z. Physik. Chem., B*, 1941, **51**, 49. [f] S. Baichelova, I. G. Druzhinin, and B. I. Imanakunov, *Zh. Neorg. Khim.*, 1967, **12**, 1381. [g] B. Menshutkin, *J. Russ. Phy. Chem. Soc.*, 1907, **39**, 102. [h] K. Abykeev, K. Sulaimankulov, and M. Ismailov, *Izv. Akad. Nauk Kirg. SSR*, 1974, 36. [i] V. F. Tarakanov, *Uch. Zap. Yarosl. Gos. Pedagog. Inst.*, 1976, **154**, 37. [j] I. A. Borukhov, T. F. Kalinevich, and A. K. Umarov, Deposited Doc. 1976, *VINITI*, 2963. [k] M. N. Nabiev, I. A. Borukhov, and O. A. Momot, *Zh. Neorg. Khim.*, 1976, **21**, 1958. [l] N. N. Gustomesova and A. S. Karnaukhov, *Zh. Neorg. Khim.*, 1974, **19**, 525. [m] B. Menshutkin, *J. Russ. Phy. Chem. Soc.*, 1909, **40**, 1415. [n] V. T. Orlova, V. I. Kosterina, and I. N. Lepeshkov, *Zh. Neorg. Khim.*, 1985, **30**, 1877. [o] V. T. Orlova, V. I. Kosterina, E. A. Konstantinova, and I. N. Lepeshkov, *Thermochim. Acta*, 1985, **92**, 709. [p] B. Murzubraimov, G. I. Shtrempler, M. Ismailov, and D. J. Altybaeva, *Zh. Neorg. Khim.*, 1985, **30**, 1896. [q] R. C. Paul, S. L. Chadha, and R. Dev, *Indian J. Chem.*, 1965, **3**, 364. [r] P. I. Kuznetzov, *J. Russ. Phys. Chem. Soc.*, 1909, **41**, 379. [s] B. Murubraimov, G. I. Shtrempler, and S. Madanov, *Zh. Neorg. Khim.*, 1985, **30**, 2438.

(iii) *Group IIIB Compounds.* The boron trihalides react with acetamide to form 1:1 adducts, by mixing solutions of the reactants in inert solvents,[137] by conductiometric titration in liquid hydrogen chloride,[67] or by absorbing boron trifluoride vapour on solid acetamide.[138,139] The bromide and chloride adducts are solids ($BBr_3{\cdot}MeCONH_2$ m.p. 98.9 °C, $BCl_3{\cdot}MeCONH_2$ m.p. 75.5—76.5 °C)[52,137] and the fluoride a colourless, non-fuming, liquid.[138] Hydrolysis occurs readily, as does pyrolysis (*e.g.* $BCl_3{\cdot}MeCONH_2 \rightarrow MeCONH{\cdot}BCl_2 + HCl \rightarrow MeCN + B(OCl)_3 + HCl$)[137] though boric acid has been claimed as a product,[138] as well as tetrafluoroborate.[139] Acetamide has also been substituted into a carboborane (7-$MeCONH_2$-7-$CB_{10}H_{12}$).[140]

Aluminium trichloride has been shown to form a 1:1 complex by density and viscosity studies in nitrobenzene solution,[141] and a 1:6 complex (white solid melting at 143 °C with decomposition) by refluxing in benzene or carbon tetrachloride.[142] Evidence for both the 1:1 and 1:6 complexes was obtained from measurements on the aqueous ternary solution,[143] as well as for mixed complexes [$Al_2Cl_6{\cdot}3MeCONH_2$, n-$C_6H_5NO_2$ when nitrobenzene was the third component;[144] $Al(OH)(OOCMe)_2(MeCONH_2)_{0.5}$ and $Al(OH)(O_2CMe)_2{\cdot}(MeCONH_2)_2$ from the quaternary $Al(O_2CMe)_3$–$MeCONH_2$–HO_2CMe–$O(OCMe)_2$ system.[145] The electrical conductivities of aluminium trichloride solutions in molten acetamide have been measured.[146] With aluminium tribromide 1:1 and 2:3 complexes were reported.[147] In molten acetamide solvolysis has been found to occur (probably at 100 °C)[91] though solutions with much more

$$AlCl_3 + 2MeCONH_2 \longrightarrow AlCl(MeCONH)_2 + 2HCl \qquad (10)$$

aluminium trichloride (only 10—30% acetamide) were found to be solvents for high molecular weight organics and polymers, and to act as solvent media for a number of reactions, alkylation, dehydrogenation, halogenation and insertion of carbonyl, sulphur, and amine groups.[148] N.m.r. (^{27}Al and ^{13}C) indicated only a 1:1 complex of low stability between acetamide and aluminium nitrate nonahydrate in heavy water.[149]

Indium trichloride solutions can be reduced electrochemically to indium

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metal[150] and have been used to form indium alloy surface layers on magnesium and aluminium alloys.[151]

Thallium trichloride was found to form 1 : 1 and 1 : 2 complexes. The latter, on the basis of infrared, molecular weight, and conductance measurements, was suggested to be dimeric with two chloride bridges between six coordinate thalliums, and the former to be tetrahedral ions (*i.e.* $[TlCl_2{\cdot}2MeCONH_2]^+$ and $[TlCl_4]^-$).[152] Thallium(I) is soluble in molten acetamide at 87 °C and has been found to behave reversibly in d.c. polarography and cyclic voltammetry.[153]

(iv) *Group IVB Compounds*. As was mentioned in the Introduction (Section 1) molten acetamide is an excellent solvent for very many organic compounds and complexes can be formed *e.g.* 2 : 1 with phenol ($2PhOH{\cdot}MeCONH_2$, m.p. 42.5 °C).[154] Phase diagrams have also been given for the potassium formate and acetate systems together with viscosity and density measurements.[155] Acetyl chloride was found to react with molten acetamide to give diacetimide $[(MeCO)_2NH]$ and the 1 : 2 hydrogen chloride complex.[3] Metal alkyl compounds solvolyse in the melt to the hydrocarbon[3] *e.g.*

$$LiBu \xrightarrow{\text{molten } MeCONH_2} Li(NHCOMe) + C_4H_{10} \qquad (11)$$

$$Zn(Et)_2 \xrightarrow{\text{molten } MeCONH_2} Zn(NHCOMe)_2 + 2C_2H_6 \qquad (12)$$

Quinones have been reduced polarographically with a two-electron step (reversibility increasing in the order benzoquinone < napthaquinone = phenanthraquinone < anthraquinone) with 1 M sodium acetate as the supporting electrolyte.[156,157] Many organic acids have been titrated in molten acetamide (98 °C) and dissociation constants have been reported.[82]

Silicon tetrafluoride was found to form an unstable 1 : 2 complex when passed into a solution of acetamide in benzene. The white crystals, initially very soluble in benzene, reacted on drying becoming insoluble in organic solvents (C_6H_6, MeCN, CCl_4, $CHCl_3$). Reaction was also indicated by the wide spread in melting point reported (105—128 °C, decomposition 220—245 °C). The infrared spectrum did not show the band shifts expected for the more usual coordination through oxygen, and nitrogen coordination was claimed by the authors.[158] A possibly important factor is that silica tetrafluoride–nitrogen bond energies are more than twice those to oxygen.[159] By contrast, silicon tetrachloride was reported to form a 1 : 4 and a

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1:8 complex (cream and light yellow in colour) but the high melting points (>240 °C) may indicate considerable polymerization.[142]

On the interaction of germanium and its compounds with acetamide, the only report is of the electrochemical behaviour of the element itself, specific conductances, streaming and zeta potentials being measured, which showed molten acetamide to be 'as electrically active as water' because of electron transfer between germanium and the melt.[160]

Tin(II) chloride was found to form a four-coordinate 1:2 complex,[161] while a probably six-coordinate di-acetamide complex with tin(IV) chloride has been reported by several groups,[54,91,142,162–166] and described as white crystals (m.p. 109 °C), as well as with tin(IV) bromide[165,167] and diphenyl tin(IV) chloride and bromide,[168] in each case the infrared spectrum indicated bonding through oxygen, though in more acidic solution an oxonium salt $[(MeCONH_3^+)_2SnCl_6]$ was formed and also studied by infrared spectroscopy.[54] Higher (1:4) complexes ($SnCl_4 \cdot 4MeCONH_2$, white crystals m.p. 61 °C, and $SnBr_4 \cdot 4MeCONH_2$, a yellow viscous liquid) have also been claimed and their conductances reported.[142] The specific conductance of the tin tetrahalide solutions and their ability to be titrated with various bases has suggested ionization to a six-coordinate diacetamide complex $[SnX_4 \cdot (MeCONH)_2]^{2+}$ may occur to some extent in molten acetamide,[91,142] though cryoscopy indicated that the complexes were undissociated in nitromethane[163] (1:1 and 1:2 breaks were found in conductiometric titration curves of $SnCl_4$ and $SnBr_4$ against MeCONHNa corresponding it is said to the formation of acid and neutral salts respectively[165]).

Tin(II) chloride solutions have been electrochemically reduced to produce alloy surface layers[151] as have lead(II) chloride solutions.[169] With lead(II) nitrate a 1:3 complex has been claimed.[170] Lead(II) cations were soluble in molten acetamide at 87 °C and the solutions have been studied by polarography and cyclic voltammetry but irreversible behaviour was reported. Lead(II) and (IV) compounds $[PbCl_2, (NH_4)_2PbCl_6]$ were found to react with basic acetamide solutions, containing sodium acetimide, to give precipitates; the amphoteric character of these and other cations varied in the order $[Sn^{II} < Pb^{IV} < Pb^{II} < Cu^{II}, Ag^{I}]$.[3]

(v) *Group VB Compounds.* Ammonium nitrate forms a low melting eutectic with acetamide (40:60 wt%, m.p. 38 °C;[171] 39:61, 38,[98] 37:63, 37.5[172]), and density,

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viscosity, and conductance measurements gave no evidence of compound formation.[173] Similar physical measurements have been made on acetamide solutions of alkali metal nitrates.[174,175] (See also Section 3Bi.) Magnesium nitrate complexes are listed in Table 2 and calcium nitrate is more than 30 mole% soluble.[176]

No reports of phosphorus compounds, other than orthophosphoric acid, have been made (*cf.* Section 3A). This acid in molten acetamide solution (at 98 °C) has been used in titrations, and its dissociation constant has been reported.[7] With arsenic, the trichloride reacted with acetamide in refluxing benzene or carbon tetrachloride solution to give a white solid 1:3 complex (m.p. 108 °C) whose conductance in molten acetamide has been measured.[142]

Antimony trifluoride solutions in molten acetamide have been electrochemically reduced to the element,[150] and antimony(III) chloride solutions have been more extensively studied, solvated protons being thought to form as well as antimony complexes.[82,177]

$$2SbCl_3 + 2MeCONH_2 \rightleftharpoons SbCl_2{\cdot}NHCOMe + SbCl_4^- + MeCONH_3^+ \qquad (13)$$

Antimony(III) bromide and iodide have only been reported to react in molten acetamide to give insoluble products.[3] Antimony(V) chloride was more acidic in molten acetamide and was found to be dibasic suggesting a 1:2 complex ($SbCl_5{\cdot}2MeCONH_2$)[165] with unusual seven-coordinate antimony. This complex, together with 1:1 and 1:5 complexes have all been claimed and stated to be white crystals m.p. 62 °C, a transparent viscous liquid 'b.p. 210—212 °C', and a dark yellow oily liquid b.p. 198 °C respectively.[54,91,142,164,165] Coordination through oxygen was suggested by the infrared absorptions.[142,164] However, reaction of antimony(V) chloride with acetamide in aqueous perchloric acid produced an oxonium salt, ($MeCONH_3^+$)$SbCl_6^-$, which crystallized.[54]

Bismuth(III) cations were found to be triacidic in molten acetamide at 98 °C by titration with acetimidate anions, the first two associations being strong and the third weak,[178] the product $Bi(NHCOMe)_3$ being only slightly soluble (pK_s = 7.9).[179] Bismuth trichloride was also reported to form a solid 1:4 complex, white in colour with a melting point over 240 °C.[142] Bismuth triiodide has been reported to give an insoluble solvate with molten acetamide.[3]

(vi) *Group VIB Compounds.* Polarographic reduction of molecular oxygen at 85 °C in molten acetamide containing 1 molar sodium acetate showed two waves. The

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first reduction was to peroxide, but some hydrogen peroxide was thought to have thermally decomposed to water and oxygen (*i.e.* to have disproportionated). The second reduction wave was to water (or hydroxide).[180–184] The density and viscosity of aqueous solutions of acetamide have been measured,[184] and density measurements on acetamide solutions of aqueous hydrogen peroxide at 70—75 °C have shown no evidence of compound formation.[185]

Sulphur tetrafluoride reacts to form bis(acetimidato)sulphur [$(MeCONH)_2S$] but only in the presence of sodium fluoride as a hydrogen fluoride acceptor.[186] Sulphur monochloride forms the same product with acetamide.[187] This product is soluble in water and has been characterized by mass and infrared spectroscopy.[186] Its melting point (221 °C) distinguishes it from its isomer [$(NH_2COCH_2)_2S$, m.p. 162 °C].[187]

Hydrogen sulphide with acetamide under 8 500 atmospheres pressure and 125—150 °C, only gave a low yield (10%) of diethyl disulphide together with elemental sulphur (19%), the major part of product being unreacted acetamide (61%).[188]

Sulphur trioxide however forms 1:1 and 1:2 complexes exothermically (described as brown or red-brown, and lemon-yellow 'sticky masses' respectively)[91,162,164] and the infrared absorptions of the former [3 410 (ν_{NH}), 1 600 (δ_{NH}), 1 380 (δ_{CH}), 1 105 (w), 1 102 (w)] were taken to indicate bonding *via* carbonyl oxygen.[164] However other reactions could have taken place and acetimidato groups may well be present. Certainly conductivity measurements in nitrobenzene solution were considered to arise by proton donation to solvent molecules.[91] Some doubt also arises about the nature of both compounds because, although the analytical results for sulphur and nitrogen were close to theoretical, they were unstable, could not be recrystallized, and decomposed 'at higher temperatures'.[142,164] Aqueous solutions with persulphate reacted when irradiated ($S_2O_8^{2-} \longrightarrow \dot{S}O_4^- \xrightarrow{MeCONH_2} {}^{\bullet}CH_2CONH_2 + HSO_4^-$).[189] No complex was found between potassium sulphate and acetamide in a phase diagram study.[190]

Lithium thiocyanate is soluble in molten acetamide to more than 26 mole%[176] and phase diagrams of acetamide with two other thiocyanates have been determined, that with the sodium salt showing an inflexion (32 mol% NaSCN at 52 °C) which may be due to a peritectic and would thus indicate compound formation, together with a eutectic (22.5 mol% at 15 °C).[191] Potassium thiocyanate showed only a eutectic (quoted as 26 mol% at 25.5 °C[191] and 24.7 mol%

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at 28.5 °C).[192] A ternary eutectic phase diagram study (acetamide–NaSCN–succinimide) has also indicated the 1:2 peritectic.[193] Binary eutectics with both sodium and potassium thiocyanate have been the subjects of a number of investigations, longitudinal and shear impedance, density and viscosity measurements having been made with acetamide–sodium thiocyanate and interpreted as suggesting (unspecified) changes in liquid structure around 23 °C; these highly viscous solutions show a strong tendency to supercool.[194–197] The anode deposits from acetamide–potasssium thiocyanate eutectic at high current densities were of insoluble orange-yellow parathiocyanogen [$(SCN)_x$] and have been shown to be photochemically active. However at low current densities, the oxidation products were soluble and suggested to be thiocyanogen and the trithiocyanogen anion [$(SCN)_2$ and $(SCN)_3^-$] though positive identification was lacking.[198,199]

Tellurium tetrachloride forms a 1:2 adduct by direct reaction in boiling benzene, or carbon tetrachloride, which was described as a 'greenish-black semi-solid',[142] whose infrared spectrum suggests coordination by oxygen,[91,200] and five coordinate tellurium (the far infrared 240 cm^{-1} band is cited as diagnostic[200]). Since its molar conductivity in nitromethane was nearly equal to that of a 1:1 electrolyte an equilibrium was postulated.

$$TeCl_4 + 2MeCONH_2 \rightleftharpoons [TeCl_3(NH_2COMe)_2]^+ + Cl^- \qquad (14)$$

(vii) *Group VIIB Compounds.* The halide anions are, as expected, stable in molten acetamide. Hydrogen fluoride solutions have been titrated and a dissociation constant reported[82] as has a 2:1 compound.[201] The complexes of hydrogen chloride were discussed earlier (Section 3A).

Of the three elements studied, acetamide has been fluorinated during electrolysis of molten potassium hydrogen fluoride at 120 °C. A variety of gaseous products were formed (NF_3, CF_4, C_2F_6, COF_2, N_2O, CO_2, N_2, O_2).[202,203] The specific conductance of bromine in acetamide has been measured,[204] and bromine is stated to interact with acetamide to form a 1:1 complex (as indicated by density,

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viscosity, and conductivity measurements in nitromethane solution[205]) which from galvanic cell studies was considered to ionize[206–209]

$$Br_2 + MeCONH_2 \rightleftharpoons MeCONH_2{\cdot}Br_2 \rightleftharpoons [MeCONH_2Br]^+ + Br^- \qquad (15)$$

though other ions ($[Br(MeCONH_2)_n]^+$ and Br_3^-) have also been postulated because the transference number of the cation is quite small.[82]

E.m.f. data indicate surprisingly that iodine in molten acetamide is less stable than bromine, the molar conductivity decreasing with dilution and increasing temperature,[209] and the infrared spectrum again suggesting coordination through oxygen.[210] Recent potentiometric and voltametric studies showed two waves in the oxidation of iodide (to I_3^- and I_2) together with a maximum (ascribed to I^+). In the absence of iodide, iodine in acetamide was again unstable and slowly reduced to iodide. However, in the presence of excess chloride, iodide was oxidized in one step to iodine dichloride (ICl_2^-).[211]

Iodine monochloride forms an adduct, suggested to be 1:2 by viscosity measurements at 25—45 °C, which has a very high conductance. The ionization

$$ICl + 2MeCONH_2 \rightleftharpoons ICl(MeCONH_2)_2 \rightleftharpoons (MeCONH_2I)^+ + Cl^- \qquad (16)$$

is suggested, since iodine was found to be discharged at the cathode on electrolysis.[212] The compound possibly dissociates (to 1:1) in nitrobenzene solution,[213] and is highly active in halogenation and oxidation reactions.[214] Hydrogen iodide is soluble in acetamide[215] and potassium iodide almost completely dissociated.[216]

Of the oxyacids, perchloric acid has been studied (see Section 3A) and lithium perchlorate solutions, all apparently stable near 80 °C[95,176] and hypobromous acid has been found to react with acetamide, initially to form a 1:1 adduct, which then dehydrated to acetimidatobromide (MeCONHBr).[217] Exchange of ^{18}O with alkali metal bromates was almost completely absent in molten acetamide at 170 °C over 25 hours, but exchange of hydrogen between acetamide and water was comparatively rapid as the latter was added. Acetamide was found to have no effect on $H_2{}^{18}O$ exchange when added to aqueous solutions of sodium and potassium bromates, as with these cations no ion pairs were considered to be formed. But it considerably reduced exchange with the lithium, magnesium,

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cadmium, zinc, copper, and nickel bromates, as with these salts the cations are thought to form ion pairs with bromate, and to have a common hydration sheath, part of which acetamide replaces.[218–220]

Astatine in oxidation states I and III (as AtX, where X = HSO_4^-, NO_3^-, ClO_4^-, or $MeCOO^-$, and as At^{3+}) does not seem to interact with acetamide (solid acetamide was contacted with n-heptane containing astatine, without significant absorption), although with other ligands (all insoluble in n-heptane) anionic or cationic complexes were formed (AtX_2^- or AtL_2^+ with At^I).[221]

C. Transition Metals.—(i) *Scandium Group.* The interactions of compounds of these metals with acetamide has been little studied, as might be expected.

However, scandium trichloride has been reported to form a 1:4 complex with acetamide, as pink crystals (m.p. 135 °C). This complex has an infrared absorption (quoted as 3 230, 3 090, and 1 660 cm^{-1}) which was 'considered to indicate co-ordination through nitrogen', but although the N–H stretching frequencies are slightly lowered, and therefore not in accord with oxygen coordination, that at 1 660 cm^{-1} (and assigned to a C–C stretch) is of a similar energy to many other amide I band absorptions (and generally considered to be largely due to C=O stretching) for oxygen bonded complexes. Part of the explanation may indeed be due to instrumental effects, since the absorptions quoted for acetamide itself (3 290, 3 138, and 1 640 cm^{-1})[222] are in fact much lower than those usually found (*cf.* Table 1).

Yttrium trichloride is also the subject of one report, a study of the ternary aqueous system (YCl_3–$MeCONH_2$–H_2O) at 30 °C indicating one compound ($YCl_3 \cdot 4MeCONH_2 \cdot 5H_2O$) but no compounds were found in analogous studies with yttrium(III) sulphate.[223]

Reactions with lanthanum and lanthanide compounds are dealt with in a later section.

(ii) *Titanium Group.* The reaction of titanium tetrachloride was initially reported in 1934[3] and later found to form a 1:1 complex (yellow, m.p. 133.4 °C) from methylene chloride solution, with an infrared spectrum indicating coordination through oxygen,[224] but a 1:1 complex obtained by direct reaction (10 hours at 60—70 °C) has been described as red with a melting point of 104 °C, though with similar infrared absorptions.[225] A 1:2 complex has been prepared by reaction in benzene or carbon tetrachloride solution and was found to form conducting solutions in molten acetamide. It was considered to have a six coordinate octa-

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[218] T. S. Kuratova, M. D. Tereshkevich, O. K. Skarre, and A. N. Baturin, *Zh. Fiz. Khim.*, 1964, **38**, 1535.

[219] T. S. Kuratova, M. D. Tereshkevich, E. E. Golteuzen, E. Y. Pozhidaeva, and O. K. Skarre, *Zh. Fiz. Khim.*, 1965, **39**, 2365.

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[222] N. L. Firsova, Y. V. Kolodyashni, and O. A. Osipov, *Zh. Obshch. Khim.*, 1969, **39**, 2151.

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[224] D. Schwartz and R. Heyer, *J. Inorg. Nucl. Chem.*, 1967, **29**, 1384.

[225] N. Yoshino and T. Yoshino, *Kogyo Kagaku Zasshi*, 1968, **71**, 1025.

hedral structure with coordination of acetamide through oxygen. This compound on titration with basic solutions (sodium acetimidate, quinoline, or α-picoline in molten acetamide) gave 1 : 1 and 1 : 2 endpoints illustrating the acidic nature of such complexes.[91,166] Solutions of titanium tetrachloride have been used for electroplating,[226,227] and solid titanium disulphide is reported to form intercalation compounds reversibly with acetamide.[228]

Zirconium tetrachloride was reported to form a 1 : 4 complex as a 'gummy solid' with a melting point of 174.6 °C. No structural details were obtained but the analogous formamide complex was claimed to have six-coordinate zirconium with coordination through oxygen and two additional amide molecules being attached through hydrogen bonds.[229] Zirconium oxydichloride however formed a 1 : 2 complex on reaction in inert solvents, with the infrared spectrum again indicating coordination through oxygen. However the complex was also reported to have an extraordinary melting point of 'over 800 °C',[230] which was elucidated in some later thermogravimetric results which stated weight loss began at 160 °C, reached a maximum rate of loss at 200 °C and dropped to zero from 415 °C[231] (*i.e.* constant weight) and thus suggesting complete loss of acetamide from this temperature. Isopropyl zirconium chlorides have been refluxed with acetamide in hexane, forming 1 : 1 complexes with monoisopropyl zirconium trichloride and with diisopropyl zirconium dichloride. Triisopropyl zirconium chloride also gave the first product $[Me_2CH)ZrCl_3 \cdot MeCONH_2]$ by disproportionation, but no adduct was formed with tetraisopropyl zirconium.[232] However, after refluxing the latter reactant with acetamide in anhydrous benzene highly polymeric products with up to four acetamides per zirconium were reported.[233] These polymers had considerable stability for they were found not to sublime under vacuum up to 250 °C, nor to decompose below 300 °C.[234]

No reactions with hafnium compounds are reported in the literature.

(iii) *Vanadium Group.* A vanadyl(IV) sulphate complex with two acetamides has been reported, the infrared spectrum indicating bonding of acetamide through oxygen and with bidentate sulphate.[235] Two vanadyl(V) compounds ($VOPO_4 \cdot 2H_2O$ and $VOAsO_4 \cdot 3H_2O$) formed intercalation compounds, the acetamide forming hydrogen bonds through the amide group.[236]

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[226] N. K. Tumanova, N. M. Sarnavikii, M. U. Prikhodko, A. V. Chetverikov, L. V. Bogdanovitch, and I. M. Mukha, *Obraztsy Tavarnye Znaki*, 1981, **40**, 112.

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[232] Y. Nario and T. Yoshino, *Kogyo Kagaku Zasshi*, 1969, **72**, 2293.

[233] K. R. Nadar, A. K. Solanki, and A. M. Bhandari, *Indian J. Chem., Sec. A*, 1980, 69.

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[236] M. M. Lora, L. M. Real, A. J. Lopez, S. B. Gomez, and A. R. Garcia, *Mater. Res. Bull.*, 1980, **21**, 13.

Several niobium and tantalum pentahalide adducts have been claimed (MX_5·*n*-$MeCONH_2$, where $n = 1, 2$, or 3 with $NbCl_5$, $n = 1$ or 3 with $NbBr_5$ and $TaBr_5$) with conductivity and dipole moment measurements indicating bonding through oxygen.[237] Niobium oxychloride formed a number of complexes ($NbOCl_3$·*n*-$MeCONH_2$ where $n = 2\frac{1}{2}$, 3, 4, 6, and 7) which were all 1:1 electrolytes with oxygen bonded acetamide. In ethanol another complex was formed [$NbOCl_2(OEt)(MeCONH_2)_4(EtOH)$].[238] The niobium and tantalum disulphides form many intercalation compounds (up to $2MS_2 \cdot MeCONH_2$) when heated with acetamide in the absence of air.[239]

(iv) *Chromium Group.* Of chromium(VI) compounds, chromates, and chromium trioxide were early reported to be 'slowly reduced', though no further details were given.[1] Much later chromyl chloride was reacted with acetamide in carbon tetrachloride solution to give a 'brown sticky mass' which nevertheless yielded surprisingly good analytical results corresponding to a 1:2 adduct, the infrared spectrum showing band shifts indicative of coordination by oxygen.[240]

Chromium(III) perchlorate was found to form a 1:6 complex, whose visible–ultraviolet spectrum in nitrobenzene solution [absorption bands at 16 450 cm^{-1}, molar extinction coefficient 53.0 l mol^{-1} cm^{-1}, assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ transition; and 22 940 cm^{-1} (41.3) to $^4A_{2g} \rightarrow {}^4T_{1g}(F)$] suggested octahedral coordination by the acetamide oxygens.[241] (These values of the spectroscopic parameters have been much quoted in data compilations,[242,243] and indicate that the ligand field of acetamide is slightly less than that of water but greater than those of urea or DMSO, the D_q values for these four ligands being 1 645, 1 740, 1 600, and 1 577 cm^{-1} respectively). When an anion more coordinating than perchlorate was present less acetamide was found to be coordinated, for example with thiocyanate only two acetamides per chromium [$KCr(SCN)_4(MeCONH_2)_2$, m.p. 208 °C (d), was separated from a solution of $KCr(SO_4)_2 \cdot 12H_2O$ with excess KSCN and $MeCONH_2$]. The molar conductivity of this compound (139 in acetone) indicates the presence of two ions, while infrared and electronic spectroscopy showed reversal (at least in part) of the thiocyanate coordination from nitrogen, which is usual with chromium(III), to sulphur bonding. The absorptions of coordinated acetamide quoted indicated bonding through oxygen.[244]

Acetamide forms an aqueous insoluble 'reineckate' in 0.5 M hydrochloric acid (of composition $MeCONH_3^+[Cr(NH_3)_2(NCS)_4]^-$) which decomposes at 136—8 °C. Most nitrogen bases form similar salts which are used as a basis for their forensic

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[237] J. R. Masagner Fernandez and M. R. Bermejo, *Ann. Quim.*, 1973, **69**, 1099.

[238] S. M. Sinitsyna and N. A. Razorenova, *Koord. Khim.*, 1985, **11**, 617.

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[241] R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, 1963, **2**, 124.

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[243] M. Ban and J. Csaszar, *Acta Chim. Acad. Sci. Hung.*, 1967, **54**, 133.

[244] G. Contreras and R. Schmidt, *J. Inorg. Nucl. Chem.*, 1970, **32**, 127.

identification and separation.[245] Acetamide has also been substituted for cyclopentadiene in chromocene.[246,247]

Chromium(III) chloride solutions in molten acetamide have been used for chromium plating, solutions of chromium(III) acetate having a lower conductivity.[248]

Molybdenum compounds appear not to have been studied but for the report of a molybdenyl(VI) complex formed by 'lengthy ageing', presumably hydrolysis, of an acetonitrile solution $[MoCl_4(NO)(MeCN)_4$ in $MeCN \rightarrow MoO_2Cl_2(MeCONH_2)_2]$.[249]

Tungsten hexachloride in ether solution is reported to form a 1:6 complex which is greenish-yellow in colour, is insoluble in common organic solvents, and decomposes in moist air.[250] Tungsten oxyfluoride in acetonitrile solution however gave a 1:1 complex, considered from its infrared and Raman spectra to be *trans* octahedral and oxygen bonded.[251] In contrast tungsten(VI) oxychloride in carbon disulphide, when mixed with acetamide dissolved in benzene was reported to give a 1:4 complex of 'dirty grey' colour and of 'considerable stability'. Chlorides were considered to be displaced by oxygen-bonded acetamides ($[WO(MeCONH_2)_4]Cl_4$).[252]

(v) *Manganese Group.* Manganese(II) chloride was early reported to be highly dissociated in acetamide solution including the original water of hydration,[216] and later a 1:2 complex was observed to form on direct reaction in refluxing benzene or carbon tetrachloride, the light pink crystals (m.p. 188 °C)[142] having infrared and Raman spectra indicative of oxygen coordination.[253] The heat of formation has been calculated from solution data.[254]

Phase diagram studies on aqueous acetamide solutions indicated a number of complexes with manganese(II) halides ($MnCl_2 \cdot 2MeCONH_2 \cdot H_2O$; $MnCl_2 \cdot 4MeCONH_2 \cdot H_2O$; $MnBr_2 \cdot 4MeCONH_2 \cdot H_2O$; and $MnI_2 \cdot 4MeCONH_2$),[255] and with manganese(II) acetate [$Mn(O_2CMe)_2 \cdot MeCONH_2 \cdot H_2O$; $Mn(OOCMe)_2 \cdot 2MeCONH_2$] where *X*-ray diffraction and infrared spectra showed the complexes to be octahedral with oxygen-bonded acetamide and bidentate acetate.[256] However with manganese(II) nitrate an anhydrous 1:6 complex $[Mn(NO_3)_2 \cdot$

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[245] L. Kum-Tat, *Anal. Chim. Acta*, 1961, **24**, 397.

[246] L. Benes, J. Kalousova, and J. Votinsky, *J. Organomet. Chem.*, 1985, **290**, 147.

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[254] M. S. Barvinok and L. V. Mashkov, *Zh. Neorg. Khim.*, 1985, **30**, 2972.

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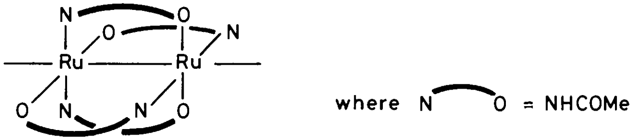
[256] O. F. Khadzhaev, T. A. Azizov, and A. N. Parpiev, *Koord. Khim.*, 1977, **3**, 1495.

$6MeCONH_2]$ forming triclinic crystals has been prepared,[257] as have two hydrated complexes $[Mn(NO_3)_2{\cdot}6MeCONH_2{\cdot}2H_2O$ and $Mn(NO_3)_2{\cdot}4MeCONH_2{\cdot}2H_2O]$ which were again oxygen bonded to manganese.[258]

No compounds of technetium or rhenium containing acetamide appear to have been prepared.

(vi) *Iron Group.* An iron(II) chloride complex $(FeCl_2{\cdot}2MeCONH_2)$ was made by the unusual route of reaction of an iron carbonyl, $Fe_3(CO)_{12}$, with acetamide in chloroform [possibly a $Fe(CO)_3(MeCONH_2)_2$ intermediate was first formed between the carbonyl and acetamide, which then reacted further with chloroform] which was initially considered to be monomeric and tetrahedral.[259] Later intensive Mössbauer spectroscopy and magnetic measurements showed the structure to be octahedral and polymeric, perhaps with chloride bridges.[260,261] There was agreement however that the acetamide was bonded through oxygen.

With iron(III) chloride a 1:3 complex has been obtained by two groups. The compound, prepared in benzene or carbon tetrachloride, was yellow-brown (m.p. 79 °C),[142] infrared and Raman spectroscopy showing oxygen bonding and hence presumably monomeric octahedral molecules.[253]



(1)

The only report on ruthenium chemistry described the reaction of a dinuclear ruthenium acetate chloride, $Ru_2(OOCMe)_4Cl$, with molten acetamide, to form a product also with the ruthenium atoms in formally different oxidation states [*i.e.* $Ru_2(NHCOMe)_4Cl$] which the authors stated might in the solid consist of dimeric units (1) with chloride bridges forming zigzag chains. Electrochemistry in several non-aqueous solvents brought about oxidation of the initially (II, III) units to (III, III) units $[Ru_2(NHCOMe)_4]^{2+}$ or reduction to (II, II) units $[Ru_2(NHCOMe)_4]$ and possibly to (I, II) units $[Ru_2(NHCOMe)_4]^-$.[262] Unfortunately vibrational spectroscopy was not undertaken and so no further information is available on this potentially most interesting family of complexes.

Of the osmium compounds reported, one was a carbonyl hydride cluster with an acetimidate group $[Os_3(CO)_{10}H(NHCOMe)]$, made by the reaction of acetamide with the osmium carbonyl acetonitrile complex in refluxing cyclohexane and characterized by elemental analysis and mass spectroscopy. Infrared spectroscopy showed, besides nine bands assigned to carbonyl absorptions, one band at 1 576 cm^{-1}, in accord with nitrogen-bonded acetimidate. The suggestion was made that

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[257] M. Nordelli and L. Coghi, *Ricerca Sci.*, 1959, **29**, 134.

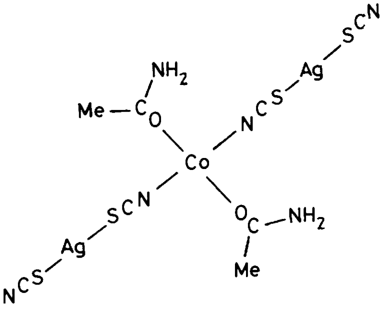
[258] V. T. Orlova, V. I. Kosterina, and I. N. Lepeshkov, *Zh. Neorg. Khim.*, 1986, **31**, 1854.

[259] P. P. Singh and R. Rivest, *Can. J. Chem.*, 1968, **46**, 1773.

[260] T. Birchall, *Can. J. Chem.*, 1969, **47**, 1351.

[261] T. Birchall and M. F. Morris, *Can. J. Chem.*, 1972, **50**, 201.

[262] M. Y. Chavan. F. N. Feldman, Y. Q. Lin, J. L. Bear, and K. M. Kadish, *Inorg. Chem.*, 1984 **23**, 2373.



(2)

the acetimidate was also coordinated through oxygen and thus bridging between two osmiums of the cluster. However, again proof that the acetimidate was bidentate and any further vibrational data are lacking.[263,264] The others all contained an anionic carbonyl hydride cluster $[(Os_4H(CO)_{12}(\mu_3\text{-}N(CO)CH_3)^-$ with $Au(PPh_3)^+$, $Cu(PPh_3)^+$, or $N(PPh_3)_2^+]$ in which the crystal structure of the first showed a N(CO)Me group bridged to two edges of the Os_4 butterfly by nitrogen.[265]

(vii) *Cobalt Group*. An early report indicated that cobalt(II) chloride dissolved in molten acetamide and was highly dissociated, but more recently a 1 : 6 complex was reported ($CoCl_2{\cdot}6MeCONH_2$), made by direct reaction in benzene or carbon tetrachloride, which was pink, and presumably octahedral, with a melting point of 58 °C.[142] Other complexes have been suggested from interfacial tension measurements on aqueous acetamide solutions ($CoCl_2{\cdot}2MeCONH_2$; and $CoCl_2{\cdot}MeCONH_2$)[135] but obviously water could also be coordinated. The heat of formation has been calculated for the 1 : 2 complex.[254]

Direct reaction of cobalt(II) perchlorate in acetone/ether solution also gave a 1 : 6 complex which was studied by *X*-ray powder diffraction, infrared, and reflectance spectroscopy (u.v./visible bands at 19 000, 15 200, and 7 800 cm^{-1}). Octahedral coordination by acetamide oxygens was inferred and acetamide was placed in the spectrochemical and nephelauxetic series as follows ($MeCONH_2 > MeCO_2H > CO(NH_2)_2$ and $MeCONH_2 > CO(NH_2)_2 > MeCO_2H$ respectively.[266] The same 1 : 6 complex was deduced from phase diagram studies of the ternary system $Co(ClO_4)_2\text{–}MeCONH_2\text{–}H_2O$ and it was found to lose some acetamide above 143 °C, to melt at 198 °C, and to decompose at 278 °C.[267] These studies also indicated another mixed complex $Co(ClO_4)_2{\cdot}4MeCONH_2{\cdot}2H_2O$[267] which was presumably also octahedral with oxygen coordination of acetamide and water—although a 1 : 2 : 1 complex with cobalt(II) chloride (m.p. 62 °C) was claimed in 1886.[268] An analogous mixed complex was found in the ternary system with

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[263] B. F. Johnson, J. Lewis, T. I. Odiaka, and P. R. Raithby, *J. Organomet. Chem.*, 1981, **216**, C56.

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[267] Y. A. Goryunov, *Uch. Zap. Yarosl. Gos. Pedagog. Inst.*, 1976, **154**, 30.

[268] G. Andre, *Jahresber. Fortschr. Chem.*, 1886, 1303.

cobalt(II) nitrate at 25 °C [$Co(NO_3)_2{\cdot}4MeCONH_2{\cdot}2H_2O$, density 1.61, m.p. 89 °C, loss of water from 112 °C, explosive decomposition 226—253 °C to water-insoluble 'powder', presumably cobalt oxides], together with another complex [$Co(NO_3)_2{\cdot}6MeCONH_2{\cdot}2H_2O$, density 1.51, m.p. 96 °C, water loss from 129 °C, decomposition 229—252 °C] apparently having an anomalously high coordination, unless some acetamide was attached by hydrogen bonds.[269–272] An anhydrous 1:6 complex [$Co(NO_3)_2{\cdot}6MeCONH_2$] as triclinic crystals has also been reported.[257] With cobalt(II) thiocyanate a different stoicheiometry was found [$Co(NCS)_2{\cdot}4MeCONH_2$], where again infrared spectroscopy data suggested bonding of acetamide through oxygen and of thiocyanate through nitrogen.[253] Less coordination by acetamide was found with another cobalt(II) thiocyanate complex (2) where tetrahedral geometry was postulated on the basis of infrared measurements which indicated coordination of acetamide through oxygen, as well as bridging and sulphur bonded thiocyanate. Thermogravimetric analysis showed a three-step decomposition (equation 17).

$$Co(NCS)_2(NCSAg)_2(MeCONH_2)_2 \xrightarrow{100-400\,^\circ C} Co(NCS)_2(NCSAg)_2 \xrightarrow{500-600\,^\circ C}$$
$$Co(CN)_2 + Ag_2S \xrightarrow{1\,000-1\,150\,^\circ C} Co + Ag \qquad \text{(ref. 273)} \quad (17)$$

Similar compounds with selenocyanate and thallium thiocyanate groups (formulated as $M[Ag(SCN)(SeCN)]_2{\cdot}2MeCONH_2$ and $(MeCONH_2)_2M(NCS)_2(NCSTl)_2$ where M = Co, Ni, or Cu) have also been reported recently.[274,275] Another tetrahedral complex ([$Co(MeCONH_2)_3Cl$]Cl) has been reported recently which again has oxygen-bonded acetamide.[276] The aqueous ternary phase diagram with cobalt(II) formate indicated a further different stoicheiometric ratio [$3Co(O_2CH)_2{\cdot}MeCONH_2{\cdot}6H_2O$].[277]

Cobalt(III) complexes are much rarer with acetamide, only three being reported, even though cobalt(III) solutions [of $Co(NH_3)_5Cl_3$ and $K_3Co(CN)_6$] were early found to be deep blue. All reported complexes, however, are of considerable interest, the first (*trans* $Na[CoSO_3(DH)_2MeCONH_2$ where DH_2 = dimethylglyoxime) was unusual by having acetamide in an anionic complex and was prepared as orange rhombic crystals by treating the corresponding aquo complex with acetamide in aqueous alcohol. The coordination of the acetamide was weak however, since hydrolysis occurred immediately in dilute aqueous solution.[278] Thermo-

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[269] A. D. Dzhunusov, B. I. Imanakunov, M. K. Kydynov, and A. S. Karnaukhov, *Uch. Zap. Yarosl. Gos. Pedagog. Inst.*, 1969, **66**, 181.

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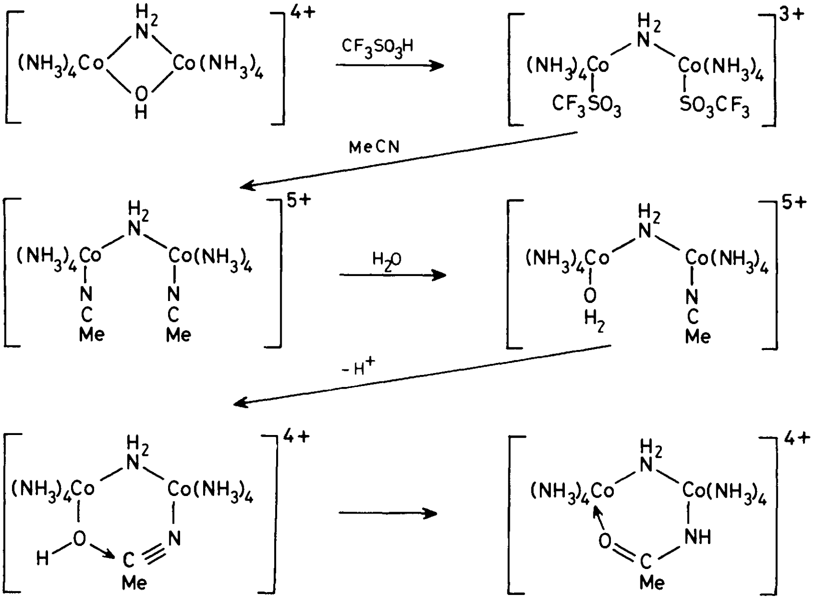

Scheme 1

gravimetry was reported later.[279] The second acetamide complex was unique in apparently having isomeric forms. It was formed from an acetimidate complex of cobalt(III) ($[\text{NH}_3)_5\text{CoNHCOMe}](\text{ClO}_4)_2$) which was itself made by heating the aquo pentammino cobalt(III) complex with acetamide in trimethyl phosphate solution, and was shown to be bonded to nitrogen by *X*-ray single crystal diffraction[280] and by proton magnetic resonance.[281] Treatment of the acetamidate complex with perchloric acid gave an acetamide complex ($[(\text{NH}_3)_5\text{CoNH}_2\text{COMe}](\text{ClO}_4)_2$) which as would be expected had very different ultraviolet absorptions [29 300 cm^{-1} (57.5 l mol^{-1} cm^{-1}) and 21 000 (61.5) as compared to 40 000 (2 400), 28 500 (83.5) and 20 600 (71.1) for the acetimidato complex][281] and was highly acidic ($\text{p}K_a$ (25 °C) 2.16 compared to 14 at 20 °C for acetamide).[282]

Interestingly, this orange nitrogen-bonded complex underwent conversion in the solid into the pink oxygen-bonded complex.[281,283]

The third complex was of binuclear cobalt(III) with a bridging amide anion (NH_2^-) which was also bridged by an acetimidate anion coordinated through both nitrogen and oxygen, which had been formed by hydrolysis of an acetonitrile complex.[284] The reaction was thought to proceed as shown in Scheme 1.

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[279] N. N. Chaban, G. P. Syrtsova, G. B. Seifer, and N. M. Thu, *Koord. Khim.*, 1977, **3**, 582.

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[281] R. J. Balahura and L. Hutley, *Can. J. Chem.*, 1973, **51**, 3712.

[282] R. J. Balahura, *Can. J. Chem.*, 1974, **52**, 1762.

[283] R. J. Balahura and R. B. Jordan, *J. Am. Chem. Soc.*, 1970, **92**, 1533.

[284] N. J. Curtis, K. S. Hagen, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1984, **23**, 1571.

Rhodium(III) chloride hydrate did not react with acetamide at room temperature and on heating formed an ammine complex ($[Rh(NH_3)_5Cl]Cl_2$)[285] but binuclear rhodium(II) compounds have been the subject of considerable study. Dirhodium tetraacetate, for example, undergoes a stepwise reaction in molten acetamide at 120 °C to form a series of acetimidate complexes $[Rh_2(O_2CMe)_n(NHCOMe)_{4-n}$ where $n = 0$—$4]$ which have been oxidized electrochemically to the II,III and to the III,III binuclear complexes. The electrochemical potentials and electronic absorption spectra change uniformly both with the number of acetamide ligands and with the non-aqueous solvent used.[286–288] One such complex $[Rh_2(NHCOMe)_4 2H_2O]$ has been the subject of *X*-ray diffraction with rhodiums 2.415 Å apart and bridged by four acetimidate ligands, each rhodium having a pair of nitrogen donor atoms in a *cis* arrangement.[289] Such complexes form carbon monoxide adducts.[290] A crystal structure determination on a II,III complex $[Rh_2(NHCOMe)_4(H_2O)_2ClO_4]$ has given essentially the same geometry but with a significantly reduced distance (2.399 Å) between equivalent rhodiums.[291] The formation of the tetraacetimidate at 160 °C and its electrooxidation to rhodium(III) has been confirmed and further complexes formed of the type $Rh_2(NHCOMe)_4L_2$ (where L = pyr, H_2O, DMSO, PPh_3),[292,293] and $[Rh_2(NHCOMe)_4L_2]NO_3 \cdot H_2O$ (where L = theophylline), the crystal structure of the latter indicating stabilization by hydrogen bonding between the acetamide and oxygen of the base.[294] Rather similar complexes were formed on prolonged heating of dirhodium tetraformate with aqueous acetamide, but at room temperature a different product resulted, $Rh_2(O_2CH)_4 \cdot 2MeCONH_2$, which presumably now had acetamide as the axial ligands. Infrared spectroscopy again showed coordination through oxygen.[285,295] A carbonyl complex $[(\mu Cl)_3\{Rh(CO)Cl \cdot CH_3CONH_2\}_2Cl]$ has also been reported.[296]

No compounds of iridium with acetamide seem to have been prepared.

(viii) *Nickel Group*. Reactions involving acetamide and compounds of the elements of this group of the Periodic Table have been the most widely studied. Most of the attention has been directed towards platinum compounds, but a considerable amount has involved nickel. An early report stated that nickel(II) chloride was

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[285] R. N. Shchelokov, A. G. Maiorova, G. N. Kuznetsova, I. R. Golovaneva, and O. N. Evstafeva, *Zh. Neorg. Khim.*, 1984, **29**, 1335.

[286] T. P. Zhu, M. Q. Ahsan, T. Malinski, K. M. Kadish, and J. L. Bear, *Inorg. Chem.*, 1984, **23**, 2.

[287] M. Y. Chavan, T. P. Zhu, X. Q. Lin, M. Q. Ahsan, J. L. Bear, and K. M. Kadish, *Inorg. Chem.*, 1984, **23**, 4538.

[288] M. Q. Ahsan, *Diss. Abstr. Int. B*, 1984, **45**, 1461.

[289] M. Q. Ahsan, I. Bernal, and J. L. Bear, *Inorg. Chem.*, 1986, **25**, 260.

[290] M. Y. Chavan, M. Q. Ahsan, R. S. Lifsey, J. L. Bear, and K. M. Kadish, *Inorg. Chem.*, 1986, **25**, 3218.

[291] I. B. Baranovskii, M. A. Golubnichaya, L. M. Dikareva, A. J. Rotov, R. N. Shchelokov, and M. A. Porai-Koshits, *Zh. Neorg. Khim.*, 1986, **31**, 2876.

[292] M. Q. Ahsan, I. Bernal, and J. L. Bear, *Inorg. Chim. Acta*, 1986, **115**, 135.

[293] I. B. Baranovskii and R. E. Sevastyanova, *Zh. Neorg. Khim.*, 1984, **29**, 1786.

[294] K. Aoki, M. Hoshiro, T. Okada, H. Yamazaki, and H. Sekizawa, *J. Chem. Soc., Chem. Commun.*, 1986, 314.

[295] V. N. Shafranskii and T. A. Malkova, *Zh. Obshch. Khim.*, 1975, **45**, 1065.

[296] Y. N. Kukushkin, V. K. Krylov, and M. Y. Romanov, *Zh. Obshch. Khim.*, 1983, **53**, 867.

soluble in molten acetamide and was highly dissociated, the water originally coordinated to nickel being displaced.[216] Much later the electronic spectroscopy of these pale green solutions showed octahedral coordination of nickel(II) at 85 °C [the absorptions being 7 800(44), 12 800(3.9), 14 200(0.9), and 23 700(10) cm^{-1}] with an increasing shift to tetrahedral coordination (and a bluer solution) as the temperature was increased to 172 °C. The low-temperature spectrum was stated to be very like that of an acetamide aquo complex, $[Ni(MeCONH_2)_4(H_2O)_2]Cl_2$, in ethanol,[297] a complex itself made from anhydrous nickel(II) chloride and acetamide in absolute ethanol (the authors draw attention to the formation of the hydrate even though 'superficially dry conditions were maintained'[298]). Infrared studies showed this complex to involve bonding through oxygen and an *X*-ray structural analysis indicated six oxygens coordinated to nickel at virtually equal distances.[299]

A green hexaacetamido complex has been made from nickel(II) perchlorate in acetone/diethyl ether solution and its reflectance spectrum showed three main absorption bands [8 730, 13 800 (sh), 14 800, 21 800 (sh), and 25 100 cm^{-1}] with a pronounced shift to higher energies.[266] The preparation of this complex had been attempted earlier but only an oil had been obtained,[241] due it was later claimed to the presence of water, and overcome by the addition of a large concentration of ethyl orthoformate as a dehydrating agent.[266] However, an acetone solution of the oil gave three absorption bands [8 240 cm^{-1}, assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$; 13 370 $^3A_{2g} \rightarrow {}^3T_{1g}(F)$; 14 700 (sh); 24 510, $^3A_{2g} \rightarrow {}^3T_{1g}(P)$] which were again of higher energy than those of molten acetamide solution, but which might be attributed to a partially aquated nickel complex. A re-examination of the electronic spectra of nickel(II) with acetamide ligands, together with scrupulous attention to purity and water content, is obviously very desirable.

A solid hexaacetamide nickel(II) chloride complex (m.p. 66 °C) has been reported to be made by refluxing the components in benzene or carbon tetrachloride. Unfortunately no spectroscopy was carried out, but the solid complex was said to be blue in colour,[142] possibly indicating a packing effect. Nevertheless, a light green hexaacetamide with tetrafluoroborate anions has been reported with a magnetic moment of 3.49 BM, which is normal for octahedral coordination, and with infrared absorptions characteristic of oxygen-coordinated acetamide and ionic tetrafluoroborate.[166,300] A triclinic 1:6 complex with nickel(II) nitrate has also been claimed[257] and a 1:4 complex with nickel(II) thiocyanate whose vibrational spectra indicated bonding of acetamide through oxygen and of thiocyanate through nitrogen, suggesting an octahedral stereochemistry.[253] The hexammine nickel(II) bromide complex $[Ni(NH_3)_6Br_2]$ dissolved in molten acetamide to give an intensely green solution, according to an early report.[301] Spectroscopy would be interesting in order to decide if there had been ligand displacement by acetamide. Polarography and cyclic voltammetry have shown the

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[297] M. E. Stone and K. E. Johnson, *Can. J. Chem.*, 1971, **49**, 3836.

[298] M. E. Stone and K. E. Johnson, *Can. J. Chem.*, 1973, **51**, 1260.

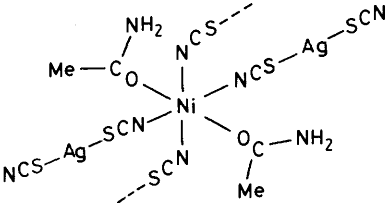
[299] M. E. Stone, B. E. Robertson, and E. Stanley, *J. Chem. Soc. A*, 1971, 3632.

[300] R. C. Paul, P. Kapila, A. S. Bedi, and S. K. Vasisht, *J. Indian Chem. Soc.*, 1976, **53**, 768.

[301] L. F. Yntema and L. F. Audrieth, *J. Am. Chem. Soc.*, 1930, **52**, 2693.

reductions of nickel(II) cations in molten acetamide to be irreversible.[153] The heat of formation of a 1:2 complex has been calculated.[254]

Aqueous acetamide complexes have also been prepared from the ternary systems. A 1:2:1 complex with nickel(II) chloride was claimed at a very early date (1886),[268] while with nickel(II) nitrate two complexes $Ni(NO_3)_2{\cdot}4MeCONH_2{\cdot}2H_2O$ and $Ni(NO_3)_2{\cdot}6MeCONH_2{\cdot}2H_2O$) were found by phase diagram studies on which DTA and TGA were carried out (melting being at 89—98 and 80—90 °C respectively, loss of water at 112 °C and 111 °C, and decomposition to water-insoluble products at 260—294 and 220—298 °C).[263,269,270,272] An aquo complex of the first of these stoicheiometries was also made by partial dehydration of the hydrated nickel(II) salts in methanol or butanol with a four times excess of acetamide, as well as with nickel(II) chloride, bromide, and iodide. These compounds had a visible spectrum suggesting distorted octahedral coordination, and significantly the octahedral splitting ($10\ D_q$) varied with the anion, so some interaction between anion and nickel was occurring. Electrical conductivities suggested the stability constants were in the order $Cl^- > Br^- > I^- > NO_3^-$.[302] Again the infrared absorptions indicated bonding of acetamide by oxygen.[270,302] Spectral and conductiometric measurements on the chloride have also been made independently.[297,298] A more unusual octahedral complex was claimed with a nickel(II) thiocyanate, which infrared measurements showed had bridging and sulphur-bonded terminal thiocyanate with oxygen-bonded acetamide (3). This structure was thus plainly polymeric though claimed as 'monomeric'. (However, a molecular weight was not determined because of 'insolubility in common organic solvents' and 'low solubility in DMSO'. Molar conductance values were quoted for the latter solution which indicated only a small concentration of ions to be present.[273])



(3)

Only three palladium–acetamide complexes have so far been reported. Palladium(II) (as K_2PdCl_4) reacts directly with acetamide to give an acetamidate product, $Pd_4(MeCONH)_7(OH)_2$, which is polynuclear and appears to have partially oxidized metal centres according to infrared, n.m.r., and e.s.r. spectroscopic measurements.[303] A dipalladium complex has been claimed as the final product of a facile hydration of acetonitrile in the presence of a skilfully designed ligand. The ease of hydration under very mild conditions was considered to arise

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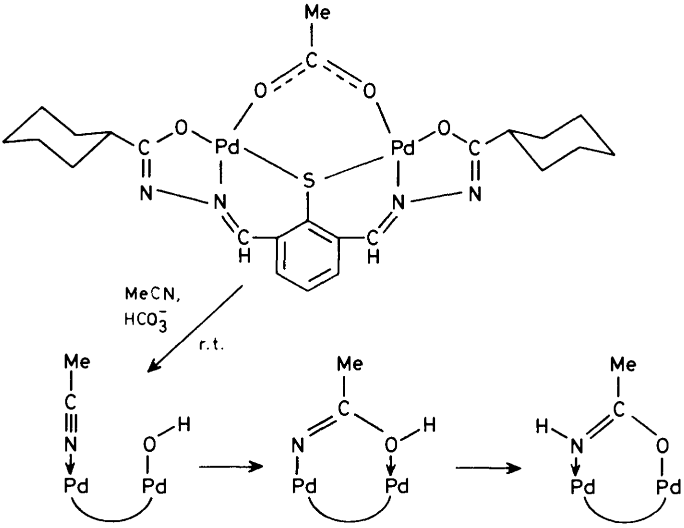
[302] M. A. A. Beg and M. R. Farooqui, *Pak. J. Sci. Ind. Res.*, 1971, 14, 336.

[303] S. Durand, G. Jugie, and J. P. Laurent, *Transition Met. Chem.*, 1982, 7, 310.



Scheme 2

because of activation of acetonitrile to nucleophilic attack when coordinated to one palladium combined with the reactant nucleophilic hydroxide, being held in close proximity and bound to the second palladium.[304] The reaction was considered to proceed as shown in Scheme 2.

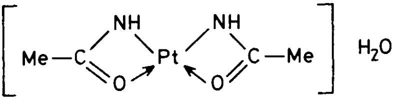
A 1:4 complex, $[Pd(MeCONH_2)_4](BF_4)_2$, has been prepared and the solid has been shown to be easily reduced to black palladium by carbon monoxide, thus having potentiality as a visual detector.[305] Such complexes can also act as sulphur dioxide and ozone detectors.[306]

The small amount of known palladium chemistry contrasts markedly with the very large number of papers on platinum acetamide complexes. The massive interest in this area arises because 'platinum blues' are important anti-cancer drugs which act by interfering with cell division. Most now contain acetamide derivatives, though the earlier and extremely financially successful drug 'cisplatin' [*cis*-$Pt(NH_3)_2Cl_2$] did not.

The numerous papers on platinum–acetamide complexes are unfortunately frequently mutually contradictory and, since general agreement has not been reached on many points, their findings will now be considered on a broadly chronological basis. One of the first reports, in 1908, was of a preparation when a platinum(II) nitrile complex was hydrolysed in the presence of silver nitrate (or sulphate) to a deep blue acetimidato complex [written as $Pt(NHCOMe)_2$ and called 'platinblau'] considered to contain platinum(II) since, besides the stoicheio-

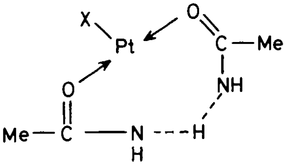
[304] M. Louey, C. J. McKenzie, and R. Robson, *Inorg. Chim. Acta*, 1986, **111**, 107.
[305] J. L. Lambert, Y. L. Liaw, J. V. Paukstelis, and Y. C. Chiang, *Environ. Sci. Technol.*, 1987, **21**, 500.
[306] Y. L. Liaw, *Diss. Abstr. Int. B*, 1986, **47**, 167.

metry, the acetamide could be replaced on treatment with concentrated hydrochloric acid and potassium chloride to give potassium tetrachloroplatinate(II).[307] The same acetimidato stoicheiometry was also claimed when the latter complex was treated with aqueous acetamide.[54] However a hydrate (4) with platinum four-



(4)

coordinated with both nitrogen and oxygen from bidentate acetimidate had earlier been claimed from this same reaction [and also from that of *cis*-$Pt(NH_3)_2Cl_2$ with acetamide][308] and an unusual three-coordinate platinum(II) hydrogen-bonded complex (5) (where X = Cl^-, I^-, NO_2^-, NO_3^-, or SCN^-).[309] Ammine complexes



(5)

{$[Pt(MeCONH_2)(NHCOMe)NH_3]X$, where X = Cl^-, Br^-, I^-, or NO_3^-, and also the corresponding compounds with en replacing NH_3} which were potentially four-coordinated, were also claimed. All these latter compounds were highly resistant to oxidizing agents, though less so than the non-electrolytes, but on treatment with chlorine, platinum(IV) complexes were formed {*e.g.* brick red $H[Pt(MeCONH_2)(NHCOMe)enCl_4]$ from $[Pt(MeCONH_2)(NHCOMe)en]X$} whose electrical conductivity indicated four ions[310] and thus possibly an interesting six-coordinate structure, but certainly deserving of further study. Alternatively, treatment with bromine gave a red compound $NH_4[Pt(MeCONH_2)Br_5]$, but prolonged boiling with *aqua regia* apparently only produced the platinum(II) complex $[PtMeCONH_2(NHCOMe)Cl]$.[310]

The acetimidato hydrate $Pt(NHCOMe)_2H_2O$ was later claimed to be polymeric by its chemistry and spectroscopy (a distinct red-blue dichroism was found, similar to other complexes with Pt–Pt interactions in chains) with the water incorporated into the crystal by hydrogen bonding.[311] An extensive investigation then

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[307] K. A. Hoffmann and G. Bugge, *Ber. Bunsenges. Phys. Chem.*, 1980, **41**, 312.

[308] I. I. Chernyaev and L. A. Nazarova, *Izv. Sekt. Platiny Drugikh Blagorodn. Met. Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR*, 1951, **26**, 101.

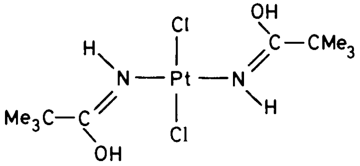
[309] I. I. Chernyaev and L. A. Nazarova, *Izv. Sekt. Platiny Drugikh Blagorodn. Met. Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR*, 1952, **27**, 175.

[310] I. I. Chernyaev and L. A. Nazarova, *Izv. Sekt. Platiny Drugikh Blagorodn. Met. Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR*, 1955, **30**, 21.

[311] R. D. Gillard and G. Wilkinson, *J. Chem. Soc.*, 1964, 2835.

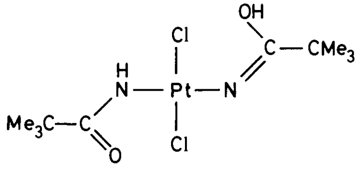
showed[312,313] that the original 'platinblau' contained much silver sulphate as well as chloride, and that it could be purified by chromatography. A related compound, $Pt(NHCOMe)_2Cl_2$, also deep blue in colour was prepared by reacting the nitrile complex $Pt(MeCN)_2Cl_2$ with molten acetamide in contact with air. Unfortunately these blue solids were amorphous, as were most of the analogous compounds prepared from substituted acetamides. However one compound, $Pt(Me_3CCONH_2)_2Cl_2$, was crystalline and a single crystal suitable for *X*-ray diffraction analysis was obtained. A partial refinement showed a non-linear chain of three platinum atoms each attached to two chlorides but did not give the positions of the light atoms. Then, however, chromatography was employed which showed the presence of three distinct compounds. On the basis of n.m.r. and infrared measurements these were considered to have the structures (6)—(8).

yellow, Pt^{II}



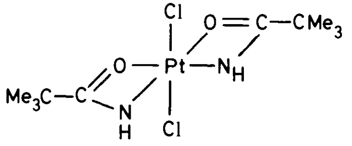
(6)

yellow, Pt^{IV}



(7)

deep blue, Pt^{IV}



(8)

The triplet chain of three platinums in the original blue-green needles is made up of either compounds (7) or (8) randomly at the centre, with compound (6) on either side, and is apparently not constrained together by more than packing considerations in the mixed crystals. The blue compound (8) was considered to be the model for platinblau, which would thus also be a platinum(IV) complex, since analysis of the chloride-free material agreed 'almost perfectly' [with $Pt(MeCONH_2)_2(OH)_2$] and moreover mass spectroscopy showed the molecular weight of the parent ion to be 345 as calculated, rather than the 329 required for the hydrate originally postulated. However, no evidence was advanced that these molecules might not be

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[312] D. B. Brown, M. B. Robin, and R. D. Burbank, *J. Am. Chem. Soc.*, 1968, **90**, 5621.

stacked in the crystal.[312,313] Shortly afterwards repetition of the chromatographic separation was reported to yield two blue phases[314] and not two yellow and one blue as originally reported. These findings do not appear to have been further elaborated.

Polymeric structures were however soon supported, together with the new suggestion that platinum had fractional oxidation states, the latter on the basis of titration with vanadium(II). Platinum–platinum interaction was considered to be diminished due to the greater metal–metal distances with nitrogen-substituted acetamides, where only yellow complexes had been obtained {*cis*-$[Pt(NH_3)_2(H_2O)_2]SO_4$ reacted with a three-times excess of acetamide to give an orange-red compound, 20 800 cm^{-1}}.[315] The blue compound precipitated from aqueous acetamide by other workers [$K_2PtCl_4 \rightarrow Pt(NHCOMe)_2Cl$] was also considered to be polymeric with platinum wholly or partially in oxidation state III; infrared analysis indicated coordination by nitrogen as well as by oxygen.[303,316] Many similar compounds with other anions (Br^-, I^-, SCN^-, NO_2^-, NO_3^-) replacing chloride were also prepared; dimeric structures were suggested with the two metal atoms joined by four bridging acetimidato groups.[317]

In another investigation the same reactants were reported to give a further deep blue compound in which planar *cis*-$Pt(MeCONH_2)_2(OH)Cl$ units, with three Pt–O bonds, were stacked to form polymers.[318] The analysis figures reported do not support this stoicheiometry, but suggest instead $Pt_2C_6H_{12}N_2O_3Cl$—or close to that expected for the acrylamide complex also claimed in this paper. The quoted analysis figures for the latter are much nearer, but not close to, those calculated for the acetamide–platinum complex. Thus the stoicheiometry of the acetamide–platinum complex may well not be that claimed. Dimers rather than indefinite polymers were thought more probable by other authors, the diamagnetic measurements suggesting variable oxidation states (*i.e.* Pt^{II}–Pt^{IV} rather than Pt^{III}).[319] At about this time titrations with cerium(IV) indicated an average oxidation state of 2.25,[320] and provided support for the chain of *four* platinums postulated by analogy with that found in a single crystal *X*-ray diffraction study of *cis*-diammine platinum α-pyridone blue $[Pt_2(NH_3)_4(C_5H_4ON)_2]_2(NO_3)_5$, which is another rare example of a crystallizable compound from this family of platinum blue compounds. Extensive *X*-ray photoelectron spectroscopy (XPS) measurements have however been made on many of these compounds, and the acetamide complex was found to have similar binding energies to the α-pyridone complex and suggested platinum in oxidation state II, though some samples of platinblau had small

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[313] D. B. Brown, R. D. Burbank, and M. B. Robin, *J. Am. Chem. Soc.*, 1969, **91**, 2895.

[314] D. F. Cahen, *Diss. Abstr.*, 1973—4, **34B**, 4266.

[315] C. M. Flynn, T. S. Viswanathan, and R. B. Martin, *J. Inorg. Nucl. Chem.*, 1977, **39**, 437.

[316] S. Durand, G. Jugie, and J. P. Laurent, *C. R. Acad. Sci., Ser. C*, 1980, **290**, 145.

[317] R. N. Shchelokov, A. Y. Tsivadze, A. G. Maiorova, and G. N. Kuznetsova, *Zh. Neorg. Khim.*, 1978, **23**, 1036; 1979, **24**, 1279.

[318] G. Schmuckler and B. Limoni, *J. Inorg. Nucl. Chem.*, 1977, **39**, 137.

[319] V. I. Nefedov, Y. V. Salyn, and I. B. Baranovskii, *Zh. Neorg. Khim.*, 1980, **25**, 216.

[320] J. K. Barton, C. Caravana, and S. J. Lippard, *J. Am. Chem. Soc.*, 1979, 7269.

amounts of higher oxidation state contaminants.[321] Other XPS (ESCA) measurements have also indicated equivalent platinums,[322,323] though the assertion that these were in oxidation state III[323] is ill-founded, since the overlap of Pt $^4J_{7/2}$ binding energies is such that oxidation states II and IV are not excluded.

In contrast, magnetic susceptibility studies further supported the suggestion of one unpaired electron per tetramer chain (*i.e.* OS 2.25) and single-crystal e.s.r. studies indicated this resided in a molecular orbital derived from atomic d_{z^2} orbitals, directed along the platinum chain axis. The visible blue colour results from a broad absorption band centred at 14 500 cm^{-1} with an extinction coefficient around 1 300 M_{Pt}^{-1} cm^{-1}, and attributed either to an amide, to metal charge-transfer,[313] or alternatively to platinum–platinum interactions.

To sum up, it is clear that platinum blues are by no means completely characterized and that further investigation is to be welcomed. However, despite this, it seems likely that there are platinum–platinum interactions and that the oxidation state is greater than two. Further, it may be that polymeric and dimeric structures are interconvertible, though experimental conditions for this have not been defined.

Some organometallic complexes, possibly somewhat similar to platinum blues but with platinum also bonded to carbon, have been made by hydrolysis of organometallic nitrile complexes (equation 19).[324–326]

$$[PtR(NCMe)L_2]BF_4 \xrightarrow{KOH} Pt(NHCOMe)RL_2 \qquad (19)$$

$$\text{where } R = Me, Ph \text{ and } L = PEt_3, PMe_2Ph, PMePh_2, PPh_3$$

More generally, platinum(II) hydride complexes [*trans*-$PtHCl(PR_3)_2$ where R = MR or Et] have been shown greatly to increase the rate of hydration of acetonitrile in basic aqueous solution (as opposed to the conventional sulphuric acid-catalysed hydration), though with a different mechanism from that of the dipalladium complex. Three intermediates were identified spectroscopically [$PtH(H_2O)(PEt_3)_2^+$, $PtH(NCMe)(PEt_3)_2^+$, and $PtH(NHCOMe)(PEt_3)_2$] and proton transfer from solvated water to the coordinated *N*-carboxamide ligand was found to be rate limiting.[327]

An undoubted compound with platinum(IV) has been reported [$(MeCONH_3)_2$-$PtCl_6$, prepared from H_2PtCl_6 and aqueous acetamide in sulphuric acid solution],[54] and the probably analogous hydrate ($H_2PtCl_6{\cdot}2MeCONH_2{\cdot}2H_2O$) reported much earlier from a similar preparation was said to form fine, long golden-brown, prisms with a melting point of 83.4 °C.[328]

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[321] J. K. Barton, S. J. Lippard, and R. A. Walton, *J. Am. Chem. Soc.*, 1978, 3785.
[322] J. Salins, V. L. Nefedov, A. G. Maiorova, and G. N. Kuznetsova, *Zh. Neorg. Khim.*, 1978, **23**, 829.
[323] V. L. Nefedov and J. Salins, *Inorg. Chim. Acta*, 1978, **28**, L135.
[324] M. A. Bennett and T. Yoshida, *J. Am. Chem. Soc.*, 1978, **100**, 1750.
[325] D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, 1980, **199**, 119.
[326] D. P. Arnold and M. A. Bennett, *J. Organomet. Chem.*, 1980, **202**, 107.
[327] C. M. Jensen and W. L. Trogler, *J. Am. Chem. Soc.*, 1986, **108**, 723.
[328] R. Fricke and F. Ruschhaupt, *Z. Anorg. Chem.*, 1925, **146**, 141.

(ix) *Copper Group.* Copper(II) chloride is soluble in molten acetamide and was early reported to be highly dissociated, and in contrast to other transition metal dichlorides the hydrated water was partially retained (*i.e.* forming $CuCl_2 \cdot \frac{1}{2}H_2O$).[216] Interfacial tension measurements gave breaks indicating two complexes ($CuCl_2 \cdot xMeCONH_2$, $x = 1$ or 2).[135] Potentiometric titration of copper(II) chloride, or nitrate, in molten acetamide at 98 °C, showed the green solutions to be weakly diacidic towards acetimidate anions, forming $Cu(NHCOMe)_2$. Stability constants were calculated.[178]

Earlier phase-diagram studies of the ternary system $CuCl_2$–$MeCONH_2$–H_2O suggested the formation of an anhydrous complex $Cu(MeCONH_2)_2Cl_2$.[329–331] The same stoicheiometry which had been reported in 1886[268] was also found by a preparation involving refluxing in benzene or carbon tetrachloride with a reported melting point of 138 °C,[142] and was also prepared by precipitation from alcoholic solutions (when the product was stated to be light green, decomposing at 110 °C, magnetic moment 2.07 BM,[253,332] and 4 charge-transfer and 20 infrared bands indicated coordination through oxygen). The heat of formation has been calculated.[254] Copper(II) bromide under similar conditions gave a different stoicheiometry ($CuBr_2 \cdot 4MeCONH_2 \cdot 2H_2O$).[332] With copper(II) sulphate the ternary phase diagram ($CuSO_4$–$MeCONH_2$–H_2O) indicated no compounds,[331] but density and viscosity measurements suggested two complexes, 1:2 and 1:4.[333] A complex of 1:2 stoicheiometry has been isolated, infrared and *X*-ray diffraction showing coordination through oxygen and bidentate sulphate.[334] A later investigation however proposed a 1:1.5 complex from refluxing methanol solutions, and this light blue compound decomposed on heating at 210—240 °C to a 1:0.5 complex which lost all acetamide at 245—260 °C.[335]

An anhydrous copper(II) nitrate 1:6 complex (triclinic) has been reported[257] and a hydrated 1:6 complex $Cu(NO_3)_2 \cdot 6MeCONH_2 \cdot 2H_2O$ from phase diagram studies.[330,331] Copper(II) acetate gave a 1:1 anhydrous complex,[256,330] which may of course be dimeric as is the case with the much better known monohydrate; coordination was certainly through oxygen. Aqueous solutions gave a hydrated complex $Cu(OOCMe)_2 \cdot MeCONH_2 \cdot H_2O$.[336] A 1:1 ratio was also found with copper(II) monochloroacetate,[337] but not with tetrafluoroborate [light blue $Cu(BF_4)_2 \cdot 4MeCONH_2$, magnetic moment 2.02 BM, i.r. indicating bonding through oxygen, distorted octahedral, with weakly bonding fluoroborate in axial positions].[300] An acetimidate of copper(II) has been made, $Cu(NHCOMe)_2$, and could be titrated with excess sodium acetimidate to give a deep yellow-green anion (equation 20).[4]

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[336] T. A. Azizov, O. F. Khodzhaev, and N. A. Parpiev, *Uzb. Khim. Zh.*, 1976, 6.

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Table 3 *Solubilities of silver*(I) *salts in molten acetamide*

Solute	*Solubility constant* (K_s) at 98 °C[a]	at 87 °C[b]
AgCl	$1.95 \pm 0.05 \times 10^{-8}$	$1.9 \pm 0.5 \times 10^{-8}$
AgBr	$4.1 \pm 0.1 \times 10^{-10}$	$8.5 \pm 0.1 \times 10^{-10}$
AgI	$1.1 \pm 0.1 \times 10^{-12}$	$2.2 \pm 0.2 \times 10^{-12}$
AgSCN	$1.3 \pm 0.3 \times 10^{-8}$	

[a] S. Guist, *Ann. Chim. (Paris)*, 1969 **4**. 235. [b] M. Gusteri, V. Bartocci, and F. Castellani, *J. Electroanal. Chem.*, 1979, **102**, 199.

$$Cu(NHCOMe)_2 + 2NaNHCOMe \longrightarrow Na_2[Cu(NHCOMe)_4] \qquad (20)$$

The only copper(I) compound so far reported, $Cu(NHCOMe)PPh_3$, contains an acetamidate group and the infrared absorptions indicate coordination through nitrogen.[338]

Silver(I) nitrate was initially found to form a 1:1 complex with acetamide[170] which was confirmed by a binary phase diagram study, though no breaks were present in density, viscosity, and conductivity isotherms.[339] However, some decomposition was suspected. Reaction was later definitely found with molten acetamide at 98 °C; the brown colour initially formed underwent progressive blackening.[340] This reaction was due to the high oxidizing power of silver(I) and nitrate together, since silver(I) cations without nitrate are stable and have been titrated potentiometrically against sodium acetimidate. Breaks were found at 1:1 and 1:2 ratios, the latter stoicheiometry being claimed as brown in colour,[4] and values for the stepwise stability constants and for the acid dissociation constant of acetamide were reported.[340] In fact silver(I) cations are more solvated in acetamide than in water at 98 °C, though the solubilities determined (Table 3) were somewhat smaller than in water at 20 °C. Further coordination occurred in molten acetamide, with halide and pseudo-halide anions, and formation constants have been given.[341,342]

An early report stated that gold(III) formed a complex ($HAuCl_4 \cdot 2MeCONH_2$) as yellow needles which decomposed before melting,[328] and solutions have been found to be electroreduced in a two-electron process.[150]

(x) *Zinc Group.* Conductivity measurements have suggested that zinc(II) halides in solution in molten acetamide at 94 °C are incompletely dissociated.[4] A number of complexes have been reported. By refluxing in inert solvent a 1:2 complex with zinc(II) chloride ($ZnCl_2 \cdot 2MeCONH_2$) was obtained[142] (described as a glassy solid of m.p. 173 °C), and the same stoicheiometry was obtained by the solubility isotherm technique at 25 °C from aqueous acetamide solutions,[343] though this was

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[339] M. A. Klochko and G. F. Gubskaya, *Zh. Neorg. Khim.*, 1960, **5**, 2491.

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[342] M. Gusteri, V. Bartocci, and F. Castellani, *J. Electroanal. Chem.*, 1979, **102**, 199.

[343] I. G. Druzhinin, B. K. Dzhashakueva, N. V. Makhonina, and T. S. Kozhanova, *Zh. Neorg. Khim.*, 1982, **27**, 231.

described as triclinic crystals, density 2.10, with a melting point of 68 °C. The latter technique also suggested two orthorhombic zinc(II) bromide complexes (1:2, d. 3.16, m.p. 59 °C; and 1:3, d. 2.86, m.p. 46 °C) both with bonding through oxygen according to infrared spectra.[343] The heat of solution of the 1:2 chloride complex has been measured and the heat of formation calculated.[254] Zinc(II) nitrate forms two hydrated complexes from such solutions [$Zn(NO_3)_2{\cdot}4MeCONH_2{\cdot}2H_2O$, d. 1.51, m.p. 70—80 °C; and $Zn(NO_3)_2{\cdot}6MeCONH_2{\cdot}2H_2O$, d. 1.62, m.p. 78—85 °C].[271,272,344] The zinc(II) acetate complex $Zn(O_2CMe)_2{\cdot}2MeCONH_2$ was shown by X-ray diffraction and infrared spectroscopy to have bidentate acetate groups with monodentate acetamide coordinated through oxygen, and to be octahedral.[256] Some evidence for the formation of chlorozincate anions was found from specific conductance measurements on zinc(II) chloride dissolved in molten acetamide saturated with potassium chloride.[345] Zinc acetimidate $Zn(NHCOMe)_2$ is amphoteric, dissolving in basic molten acetamide containing excess sodium acetimidate.[3]

Cadmium(II) cations in molten acetamide at 87 °C (1M in KO_2CMe) have been studied by d.c. polarography and cyclic voltammetry, but metal deposition was not reversible.[153] The conductivity of solutions of the halides at 96 °C suggests they are incompletely dissociated,[4] but their solubilities in molten acetamide follow the same sequence as in aqueous solution ($CdBr_2 > CdI_2 > CdCl_2$).[346] Several authors from as long ago as 1886,[268] agree that an anhydrous 1:2 complex with cadmium(II) chloride is formed, though this is variously described as white crystals (m.p. >200 °C)[142] and as 'colourless, long monoclinic prisms'.[347] X-Ray diffraction investigations showed the cadmium to be four-coordinate square planar, with two acetamides and two chlorides which were nearly equidistant to neighbouring metals, thus giving an effectively octahedral geometry.[348] A complex of the same stoicheiometry has also been found through phase diagram studies.[125] The heat of solution in water of this complex, and of the corresponding bromide and iodide complexes, has been measured and their thermal decomposition has been found to occur in three stages (equation 21).[349]

$$CdX_2{\cdot}2MeCONH_2 \longrightarrow CdX_2{\cdot}MeCONH_2 \longrightarrow CdX_2{\cdot}xMeCONH_2 \longrightarrow CdX_2 \qquad (21)$$
$$\text{where } x = 0.5\text{—}0.7$$

A 1:1 cadmium(II) bromide complex has also been reported.[350,351] Infrared spectroscopy has shown that the 1:2 complexes of the three cadmium(II) halides

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[344] A. D. Dzhunusov, B. I. Imanakunov, M. K. Kydynov, and A. S. Karnaukov, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 1969, **123**, 13.

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[350] D. Usubaliev, B. Imanakunov, and P. T. Yun, *Mater. Nauchn. Konf. Posvyashch 100(Sto) Letiyu Period. Zakona D. I. Medeleeva 1969*, 31, (1970).

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and of the thiocyanate to have oxygen-bonded acetamide and halide, or pseudohalide, bridges.[352] From aqueous acetamide solutions 1:1:1 complexes were formed with cadmium(II) chloride, though not apparently with cadmium(II) bromide, but the colourless crystals were not found suitable for *X*-ray diffraction.[125,347,350]

Cadmium(II) nitrate has also been much studied. An anhydrous 1:6 complex forming triclinic crystals has been reported which decomposed thermally in two reactions (equation 22),[257,349] as well as a 1:6 hydrate ($Cd(NO_3)_2{\cdot}6MeCONH_2{\cdot}2H_2O$, d. 1.62, m.p. 82—91 °C) from phase diagram studies of the ternary system.[271,272,344] By contrast, cadmium(II) acetate formed a 1:2 complex, characterized by *X*-ray diffraction, infrared, electrical conductivity, and thermal studies, where the acetamide was bonded through oxygen and the acetate was bidentate, giving an octahedral geometry.[256,336]

$$Cd(NO_3)_2{\cdot}6MeCONH_2 \longrightarrow Cd(NO_3)_2{\cdot}2MeCONH_2 \longrightarrow Cd(NO_3)_2 \qquad (22)$$

Mercury compounds have received mention in many reports and mercury(II) acetimidate has been known since 1909 as a yellow compound (m.p. 195 °C) prepared by reacting red mercury(II) oxide with molten acetamide at 180—200 °C,[48] also prepared from reaction with aqueous acetamide.[4] The stoicheiometry $Hg(NHCOMe)_2$ was confirmed by potentiometric titration of mercury(II) cations with acetimidate anions in molten acetamide at 98 °C; the first association was strong and the second was weak.[178,179] Bonding of mercury to the imide nitrogen is clearly indicated by n.m.r. studies,[353] and single crystal *X*-ray diffraction analysis gave a structure showing discrete planar centrosymmetric molecules with mercury forming two *trans* bonds to nitrogen with two longer bonds to the oxygens of neighbouring acetimidate anions (thus chelation does not occur) with further linking by hydrogen bonds along the *c* axis.[354] Voltammetry in molten acetamide solutions at 87 °C containing 1M potassium acetate produced a mercury acetate complex on the surface of the mercury electrode at the anodic limit.[153] Mercury(II) was shown to be the only stable oxidation state from the voltammetric and potentiometric studies, mercury(I) being found to dissociate to grey metallic mercury and mercury(II).[179] Mercury(II) acetimidate was also reported to disproportionate in the solid or in methanol/acetone solution, but in this case the anion reacted to form free acetamide and a polymer, which was claimed to be $Hg(NCOMe)_n$. Mercury(II) halides have been found to dissociate only incompletely in molten acetamide, possibly also because of disproportionation (actually claimed for $HgCl_2$ [7]), but have also been reported to form complexes ($HgCl_2{\cdot}6MeCONH_2$, m.p. 68 °C, and $HgBr_2{\cdot}4MeCONH_2$, m.p. 110 °C; both as white crystalline solids) by reaction in benzene or carbon tetrachloride solutions.[142] Earlier, two other stoicheiometries were claimed—$HgCl_2{\cdot}MeCONH_2$, m.p. 125 °C

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[352] A. Y. Tsivadze, Y. Y. Kharitonov, G. V. Tsintsadze, A. N. Smirnov, and M. N. Tevzadze, *Zh. Neorg. Khim.*, 1974, **19**, 2621.

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and $HgCl_2 \cdot x MeCONH$, m.p. 118 °C[268]—and the 1:1 stoicheiometry ($HgCl_2 \cdot MeCONH_2$) prepared from aqueous solution has also been claimed more recently.[125] A mercury(II) cadmium(II) iodide complex[355] (given as $HgI_2 \cdot 2CdI_2 \cdot 10MeCONH_2$, m.p. 85 °C) prepared from molten acetamide could well be mixed crystals {*e.g.* $HgI_2 \cdot 6MeCONH_2$, $2[CdI_2 \cdot 2MeCONH_2]$} but no structural details have been reported. Studies have also been made of the interaction of mercury(II) chloride with acetamide in neutral and basic aqueous solution (the formation constants varied $HgCl \cdot NHCOMe > Hg(NHCOMe)_2 > Hg(OH)NHCOMe$).[356]

Mercury(II) nitrate forms a 1:2 acetamide complex which has been characterized by *X*-ray diffraction and infrared techniques, though the melting point was quoted as the wide range 54—70 °C.[271,272] The same stoicheiometry was found with mercury(II) acetate, where these techniques showed bidentate acetate and bonding through the oxygen of acetamide, resulting in octahedral coordination.[256,336]

D. Lanthanide Group.—Acetimidates of four lanthanide(III) cations, $M(NHCOMe)_3$ where M = La, Pr, Nd, or Sm, were prepared by refluxing the lanthanide(III) isopropoxide with acetamide in benzene. The complexes had the 'usual' colours (white, light green, pink, and yellow respectively) and electronic (*f–f*) absorption bands were reported for praseodymium and neodymium compounds only. Infrared absorption indicated bonding nitrogen as well as some coordination through oxygen, which may support the suggested polymerization deduced from the insolubility of these complexes in common organic solvents and melting points 'above 300 °C'. Notwithstanding the latter point, thermogravimetric analysis showed considerable weight losses above 100 °C, ammonia and 'nitrile' being evolved with the eventual formation of lanthanide oxides and oxycarbonates.[357] Several solubility isotherm (phase diagram) measurements on ternary aqueous acetamide solutions have been made. In the case of lanthanum trichloride two stoicheiometries ($LaCl_3 \cdot 5MeCONH_2 \cdot 5H_2O$[358] and $LaCl_3 \cdot 4MeCONH_2 \cdot 5H_2O$[359]) have been reported, the former also being found with cerium trichloride ($CeCl_3 \cdot 5MeCONH_2 \cdot 5H_2O$[360]) but not with the tribromide ($CeBr_3 \cdot 5MeCONH_2 \cdot 3H_2O$).[361] Erbium tribromide, however, gave an anhydrous complex ($ErBr_3 \cdot 4MeCONH_2$[362]).

Cerium(IV) sulphate gave another stoicheiometry [$Ce(SO_4)_2 \cdot 4MeCONH_2 \cdot 4H_2O$, d. 2.15] which lost water at 120 °C and also showed three other (unidentified) thermal effects between 180 and 350 °C.[363] Another study showed acetamide was oxidized by cerium(IV), the measured rates indicating that this was *via* inner-sphere cerium(IV) acetamide complexes.[364]

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A number of complexes have recently been reported containing an acetamido–borane ligand {$LnL_3(H_2O)_5$ where Ln = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu and $[Ln(pyrO)_6]L_3$ where Ln = Nd, Sm, Dy, Eu, Yb, Lu and HL = $H(B_{12}H_{11}NH_2COMe)$} which was coordinated to the lanthanide *via* oxide oxygen in the solid state. These complexes dissociated extensively in water or ethanol.[365]

E. Actinide Group.—Actinium complexes have not been reported so far and thorium(IV) has been the subject of only one investigation, when thorium(IV) sulphite tetrahydrate was reacted with molten acetamide, two complexes being found after extraction with acetone which were characterized by elemental analysis [white $Th_2(SO_3)_2(OH)_2{\cdot}MeCONH_2{\cdot}5H_2O$ and pale yellow $Th_2(SO_3)_3(OH)_2{\cdot}2MeCONH_2{\cdot}4H_2O$]. The infrared absorptions indicated bonding through oxygen. Thermal analysis showed water to be lost at 70—175 °C and 65—115 °C respectively, and acetamide at 240—330 °C and 205—250 °C with formation of thorium(IV) oxide and sulphate (probably air was the oxidant) with loss of sulphur trioxide above 470 °C.[366]

At first sight it is surprising that uranium–acetamide complexes with a wide variety of ligands have been the subject of so many investigations. However this interest arose largely from an early claim of the nuclear energy industry that uranium(VI) could be effectively extracted from organic solutions by aqueous acetamide, from which it could be recovered by heating.[367] Uranium(VI) oxide dihydrate reacts with acetamide in ethanol to give a 1:1:1 complex $UO_3{\cdot}MeCONH_2{\cdot}H_2O$, whose infrared spectrum suggested coordination through oxygen,[368] which decomposed thermally in two stages (at 210 °C to $UO_2(OH)(O_2CMe)$ *i.e.* oxidation of acetamide, and then at 280—300 °C to uranium oxide(s). The final stoicheiometry depended on the oxygen partial pressure. Uranyl fluoride hydrate also complexed with acetamide to give a product, $(UO_2F_2MeCONH_2)_x$, which was thought to be polymeric. Infrared and Raman spectra, laser luminescence, and thermal stability have been reported for this compound.[369–371] Uranyl chloride in methanol solutions of acetamide formed green crystals of $UO_2Cl_2{\cdot}2MeCONH_2{\cdot}H_2O$.[372] Uranyl nitrate is soluble in molten acetamide and the ultraviolet absorption spectrum at 85 °C had 18 sharp bands.[373] A 1:2 complex, $UO_2(NO_3)_2{\cdot}2MeCONH_2$, was isolated from ethanol solution which decomposed thermally above its melting point (195 °C), losing acetamide, rapidly from 220 °C and exploding at 370 °C, forming uranium(VI)

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oxide, carbon dioxide, and nitrogen. It was noted that oxygen ligands gave less stable complexes than with nitrogen ligands.[374] But in tributyl phosphate solution acetamide is bonded to uranyl nitrate, because the changes in its absorption spectrum indicate displacement of nitrate or tributyl phosphate.[375]

Uranyl sulphate formed three complexes, two in aqueous acetamide solutions of varying concentration ($UO_2SO_4{\cdot}3MeCONH_2{\cdot}H_2O$ and green $UO_2SO_4{\cdot}MeCONH_2{\cdot}H_2O$) and a further green complex ($UO_2SO_4{\cdot}2MeCONH_2$) was formed from ethanol solutions.[372] The uranyl cations in these complexes were shown to have temperature-independent Van Vleck paramagnetism.[376] Uranyl sulphite gave two different stoicheiometries ($UO_2SO_3{\cdot}1.5MeCONH_2{\cdot}H_2O$ and $UO_2SO_3{\cdot}MeCONH_2{\cdot}1.5H_2O$),[377] the latter also being claimed with smaller, to zero, proportions of water.[378] Infrared spectroscopy indicated bonding through oxygen and probably bidentate or bridging sulphite. No detailed structures were proposed, but thermal decompositions were studied.

The perhaps unexpected uranyl phosphite complexes have been made by reaction of uranyl nitrate in aqueous acetamide solutions containing phosphorous acid [greenish-yellow crystals of $UO_2(HPO_3){\cdot}MeCONH_2{\cdot}H_2O$ and $UO_2(HPO_3){\cdot}2MeCONH_2$]. Acetamide was lost at >200 °C and ultimately uranium(IV) and (VI) phosphates were formed.[379] The structure of the uranyl chromate acetamide complex $UO_2(CrO_4){\cdot}2MeCONH_2$ has been established by *X*-ray diffraction. The uranium is surrounded by a pentagonal bipyramid of oxygens, three equatorial oxygens coming from chromate and two from the acetamide molecules, which lie at ~55° to the equatorial plane, the uranyl group being linear and at right angles to this pentagon. The $(UO_2)O_5$ groups are joined into chains by chromate bridges.[380] Thermal decomposition started at 190—220 °C with loss of acetamide; the uranyl chromate which formed decomposed at >600 °C.[381] A uranyl isothiocyanate complex has also been prepared from aqueous solution [$UO_2(NCS)_2{\cdot}MeCONH_2{\cdot}H_2O$, m.p. 105 °C] which was also concluded to have a penta-cordinated uranium(VI) cation. Though acetamide was fairly readily replaced by 1:10 phenanthroline, it was more stable than the coordinated water, since dehydration occurred at 150—160 °C and decomposition at 240—420 °C.[382,383] Uranyl oxalate, however, gave an anhydrous complex ($UO_2C_2O_4{\cdot}MeCONH_2$) from aqueous solutions.[372]

Several uranium(IV) complexes have also been made. The chloride gave a 1:6

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stoicheiometry (Cs_2UCl_6 + hot acetone solution of acetamide → $UCl_4 \cdot 6MeCONH_2$) which the infrared spectrum showed had oxygen-coordinated acetamide. A more stable 1:2.5 complex was also made which was presumed to be dimeric.[384] The sulphate, however, in molten acetamide, gave a bright green 1:4 complex [$U(SO_4)_2 \cdot 4MeCONH_2$, m.p. 180 °C] which decomposed at 240—260 °C.[385] Two other complexes with ammonium cations [$(NH_4)_2U(SO_4)_3 \cdot 2MeCONH_2$ and $(NH_4)_2U(SO_4)_3 \cdot 2MeCONH_2 \cdot 4H_2O$] have also been prepared which were considered to contain octa-coordinated uranium, all the ligands bonding through oxygen.[386] Uranium(IV) bromide solutions in molten acetamide have been found to electrodeposit uranium, but at a very low current efficiency, probably because of the reactivity of uranium(III).[387]

Little work has been done with transuranic elements, but neptunium(IV) and plutonium(IV) complexes ($MCl_4 \cdot 6MeCONH_2$ and $MCl_4 \cdot 2.5MeCONH_2$ have been reported and were analogous to the corresponding uranium(IV) compounds.[384]

4 Applications

As mentioned earlier, platinum–acetamide compounds are already used as anti-cancer drugs, and there is a possible new large-scale use of acetamide eutectic mixtures in thermal energy storage.[30,388,389]

Besides these, two other areas of application are being actively considered. The first, electrodeposition, arises because molten acetamide solutions are convenient in providing high metal-cation concentrations, with an absence of hydrolytic reactions. Frequently acetamide–urea eutectics have been used to achieve even lower melting points [*e.g.* with 39 mole% $CO(NH_2)_2$, m.p. 56 °C].[390–392]

An early (1930) study showed that seven metals could be electroreduced (Zn, Cd, Pb, Sn, Co, Ni, Te) and that good quality deposits could be obtained even in the presence of small quantities of water.[301] Later, reduction of titanium(IV) chloride solutions was reported[224,227] and also reduction of solutions of chromium(VI) and (III) compounds [$K_2Cr_2O_7$, $Cr(O_2CMe)_3$]. Copper, iron, and nickel have been electrodeposited from ammonium nitrate–acetamide–urea melts.[393–395] With the less electrochemically active metals, deposition ('cementation') is possible without an externally applied current (*e.g.* $InCl_3$ and $SnCl_2$ deposit alloy layers on the surface of Mg and Al alloy substrates).[151] Surface oxide layers have also been

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produced on metals, for example steels can be anodized in alkali metal nitrate–acetamide solutions.[396]

The other potential application of acetamide solutions under investigation is in thermal batteries. In one example zinc and silver(I) chloride were selected as the reactants with a 0.1 M zinc(II) chloride in acetamide solution as the electrolyte.[107,397] Alkali metal nitrate–acetamide solutions have also been considered for battery applications with iron and cobalt electrodes.[92,102,391] The solutions have been shown to cause very little corrosion, even to inexpensive steels.[398] Such batteries with lithium anodes give high discharge rates when combined with many silver salts (13 Ag^I compounds were tested) or with cerium(IV) as cathodes.[399,400] Moderate additions of ammonium nitrate (acidic) to the acetamide–urea melts were helpful in depassivating the anode but highly acidic melts themselves reacted rapidly with the lithium.[400]

Acknowledgement.—Grateful thanks are expressed to the University of Delhi and to the University Grants Commission, New Delhi, for appointment as Visiting Scientist (January–April 1985) at the Centre of Advanced Studies Chemistry Department, Dehli University; to my host Professor H. C. Gaur; and to the British Council for a travel grant. During this sabbatical term most of the initial literature survey for this review was made.

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