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DONOR PROPERTIES OF 1-AMIDINO-*O*-ALKYLUREAS

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CONTENTS

ABBREVIATIONS

AAUH,	1-amidino-*O*-alkylurea
AMUH,	1-amidino-*O*-methylurea
AEUH,	1-amidino-*O*-ethylurea
AP^iUH,	1-amidino-*O*-isopropylurea
AB^iUH,	1-amidino-*O*-isobutylurea
AB^nUH,	1-amidino-*O*-n-butylurea
AA^iUH,	1-amidino-*O*-isoamylurea

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AMEUH,	1-amidino-*O*-methoxyethylurea
AEEUH,	1-amidino-*O*-ethoxy ethylurea
AB^{n}EUH,	1-amidino-*O*-*n*-butoxyethylurea
BigH,	biguanide
Py,	pyridine
ophen,	*ortho*-phenanthroline
dipy,	2-2′-dipyridyl
en,	ethylenediamine
glyH,	glycine
alanH,	α-alanine
CSH,	*d*(+)camphor-10-sulfonic acid
d-tartH_2,	*d*(+) tartaric acid
Ac,	acetate

A. INTRODUCTION

The ligands, 1-amidino-*O*-alkylureas, were synthesized in a chance observation arising out of experiments designed to yield a biguanide derivative[1]. Originally designated as guanylalkylureas, these compounds received a review treatment in 1961 along with guanylurea and guanylthiourea, coming in the wake of the chemistry of metalbiguanide complexes[2].

However, since 1961, many significant studies have been conducted on the syntheses, structure, kinetics of formation and the reactions of co-ordinated 1-amidino-*O*-alkylureas. The chemistry of transition metal complexes of the ligands has also been extended. The present review covers the salient aspects of all the studies to-date in the light of current views of stereochemistry and bonding in metal complexes.

B. THE LIGANDS, 1-AMIDINO-*O*-ALKYLUREAS

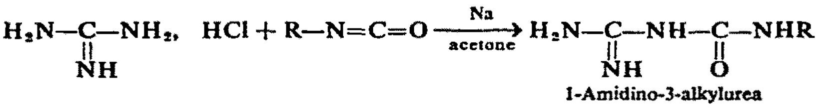
(*i*) *Syntheses, structure and general properties*

The syntheses of these ligands arose out of an attempt to prepare a biguanide derivative of methylanthranilate[1]. Since the latter was immiscible with water, ethanol was preferred as a solvent during the reaction of methylanthranilate and dicyandiamide in the presence of copper(II) acetate at reflux temperature. A deep violet solution resulted, from which a copper complex was isolated, the analysis of which did not indicate the formation of a biguanide derivative of methylanthranilate but suggested a compound resulting from the combination of dicyandiamide and ethanol. Strong resemblance of these products to copper(II) bis (guanylurea) led the authors to assume that the derivatives were ethyl substituted guanylureas. Just as in the presence of hydrogen ion a molecule of water combines with that of dicyandiamide to form a molecule of guanylurea similarly a molecule of ethanol was thought to add itself to that of dicyandiamide followed by a rearrangement to the ethylsubstituted guanylureas[1].

$$\underset{\text{Dicyandiamide}}{H_2N-\underset{\underset{NH}{\|}}{C}-NH-C\equiv N} + ROH \xrightarrow[\text{refluxed}]{Cu^{2+}} \left[\underset{\text{1-Amidino-}O\text{-alkylurea}}{H_2N-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-OR}\right] \rightarrow \underset{\text{Guanylalkylurea or 1-Amidino-3-alkylurea}}{H_2N-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-NHR}$$

This above addition reaction also occurs with other alcohols such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-amyl, isoamyl, *n*-hexyl, cyclohexyl, methoxyethyl, ethoxyethyl and butoxyethyl alcohols. Generally the copper complexes are isolated as complex acetates. These are converted to their sulphate salts from which copper is removed as the sulphide and the reagent precipitated as sulphates by the addition of acetone. In a few cases the hydrochlorides of the reagents have also been obtained by double decomposition with $BaCl_2$. With the dihydric alcohol, ethylene glycol, however, a copper complex of guanylhydroxyethylurea was obtained instead of the expected complex of ethylene-di-guanylurea[1,3,4].

A Japanese study[5] of the above template reaction followed shortly and the isolated ligands were formulated as 1-amidino-*O*-alkylethers, although no definite evidence was presented in support of this. An unambigous and independent syntheses of several 1-amidino-3-alkylureas had now been reported from the reaction of guanidine hydrochloride with an iso-cyanate in the presence of sodium and acetone[6].



$$H_2N-\underset{\underset{NH}{\|}}{C}-NH_2,\ HCl + R-N=C=O \xrightarrow[\text{acetone}]{Na} \underset{\text{1-Amidino-3-alkylurea}}{H_2N-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{O}{\|}}{C}-NHR}$$

The failure of the 1-amidino-3-alkylureas to form metal chelates in contrast to the positive reactions given by the template synthesis products identified the ligands, under review, as 1-amidino-*O*-alkylureas instead of 1-amidino-3-alkylureas. Steric hindrance offered by the alkyl group of 1-amidino-3-alkylureas prevents the —NHR nitrogen from forming bonds with metal ions[6]. Such a situation is less likely to exist in the 1-amidino-*O*-alkylureas. It is also pertinent to mention that 1-amidino-3-phenylurea obtained through the condensation of guanidine and phenylurea, also fails to furnish any metal chelates[7]. An infra-red study[8] involving amidinourea (guanylurea) and methyl and ethyl derivatives of the template syntheses reveal a strong carbonyl absorption band at 1740 cm^{-1} in amidinourea and its absence in the other two reagents. Further, amidinourea does not have any band around 1200 cm^{-1} (characteristics of C-OR stretching vibration) and at 1400 cm^{-1} (C-H symmetrical deformation vibration) but the other two ligands prominently display these very strong and sharp bands. A nickel(II) complex chloride of the methyl substituted reagent also corroborates these infra-red absorption bands. Estimation of methoxyl group of the methyl derivative gives a satisfactory positive result.[8]

Copper(II) acetate may be replaced by copper(II) chloride in the above reactions although the acetate possesses an advantage because of the higher solubility of the complex copper acetate. The apparent failure of nickel(II) acetate to bring about the alcohol addition reaction was presumed to be due to a weaker stability of the corresponding nickel complex[1]. However, this appears to be erroneous in that prolonged refluxing of nickel(II) chloride, dicyandiamide and methanol has provided the nickel(II) bis(1-amidino-*O*-methylurea) complex. These reactions are believed to be kinetically controlled[9].

Copper dicyandiamide sulphate has also been found to react with methanol providing the rose red copper(II) bis (1-amidino-*O*-methylurea) sulphate[9].

(ii) Dissociation constants

The acid dissociation constants Ka_1 and Ka_2 of several 1-amidino-*O*-alkylureas have been determined by the usual Bjerrum technique. The values ($Ka_1 \simeq 10^{-11}$) indicate a far stronger donor ability compared with amidinourea ($Ka_1 \simeq 10^{-9}$) but somewhat weaker compared with biguanides ($Ka_1 \simeq 10^{-12}$)[10,11].

C. METAL CHELATES

(i) Copper(II) complexes

Bipositive copper complexes of these ligands can be classified under three categories.

(a) Bis(1-amidino-O-alkylurea) copper(II) salts. The ligands react with aquo copper(II) ions around pH 6–7 to provide rose-red coloured complexes. The cations have been isolated in the form of a large number of salts including the iodide, thiocyanate and the thiosulphate. The solubility of the salts (*e.g.* chloride and acetate) in aqueous medium decreases with increase in the chain length of the alkyl substituent, whereas that in alcohol increases. The electrolytic conductance values in aqueous medium are in fair agreement with that for bi-univalent electrolytes. The complexes provide magnetic moment values around 1.7–1.8 B.M. The electronic absorption spectra exhibit one absorption band around 18,870–18,520 cm^{-1} which is characteristic of square planar copper(II) complexes with four nitrogen donors[14,15]. The closely related copper(II) bis(biguanide)chloride also exhibits a single absorption band[16] around 19,600 cm^{-1}. The solution absorption of these bis complexes in different solvents, namely dimethylsulfoxide, methanol and water

have been studied and the position of absorption bands have been interpreted to give the following order of tetragonality of the complexes[17,18] dimethylsulfoxide > methanol > water.

Complex	ν_{max} *in*		
	dimethyl sulfoxide	methanol	water
$[Cu(AMUH)_2](Ac)_2$	20,000–20,400 cm^{-1}	19,050–19,160 cm^{-1}	18,180–18,350 cm^{-1}
$[Cu(AEUH)_2](Ac)_2$	19,800–20,200	18,690–19,050	18,020–18,350

(b) Copper(II) bis(1-amidino-O-alkylurea). The above copper(II) salts precipitate the rose-red complex base on treatment with alkali. These complexes conform to an anhydrobase formula indicating the inner metallic characteristics of the ligands. The bases liberate ammonia on treatment with ammonium salts, providing the salts of the earlier category. These observations evidently indicate the protonation of a $—NH_2$ group that remains free even after complexation. The anhydrobases are quite stable in boiling water or aqueous alcohol, whereas the corresponding copper bases of amidinourea readily decompose[12].

(c) Copper(II) mono(1-amidino-O-alkylurea) complexes. Spectrophotometric studies of the system aquo copper(II): 1-amidino-*O*-alkylurea shows two distinct equilibria, the formation of a blue mono 1-amidino-*O*-alkylurea complex around pH 4–5 and the formation of rose-red bis(1-amidino-*O*-alkylurea) complex above pH 6:

$$[Cu(aq)]^{+2} + AAUH \overset{pH\,4-5}{\rightleftharpoons} [Cu(AAUH)(aq)]^{+2}$$
$$[Cu(AAUH)aq]^{+2} + AAUH \overset{pH\,6}{\rightleftharpoons} [Cu(AAUH)_2]^{+2}$$

Following the spectrophotometric indication of the existence of a mono complex in solution (by Job's variation), preparative studies have led to the isolation of deep blue dichloro mono (1-amidino-*O*-alkylurea) copper(II) complexes[10,12]. These complexes are, however, stable in solution only around pH 4 and readily undergo transformation to the rose-red bis complex above pH 6.

$$2[Cu(AAUH)Cl_2] \rightleftharpoons [Cu(AAUH)_2]Cl_2 + CuCl_2$$

These compounds also have magnetic moments in the range 1.7–1.8 B.M. and their electronic spectra in aqueous solution exhibit one asymmetric band around 15,380–15,100 cm^{-1}. The considerable shifting of the band towards lower frequency compared to that in the rose-red bis complexes may be interpreted in terms of a distorted octahedral structure in solution[13,19,20].

The overall instability constants of the bis complexes have been evaluated by spectrophotometric measurements. For comparison, the copper(II) complexes of amidinourea and of biguanide are included in Table-2. As is indicated by the

TABLE 1

COPPER(II) COMPLEXES OF 1-AMIDINO-*O*-ALKYLUREAS

Compound	*Colour*	*Molar conductance in aqueous medium mhos cm² mole⁻¹*	*Electronic spectra*		*Magnetic moment (B.M.)*	*Ref.*
			ν, cm⁻¹	*ε*		
$[Cu(AMUH)_2]Cl_2$	rose-red	242.8	18,515	43	1.65*	12
$[Cu(AEUH)_2]Cl_2$	rose-red	258.4	18,515	43	1.79*	12
$[Cu(AMUH)Cl_2]$	blue	—	15,150	32	1.71	12, 4
$[Cu(AEUH)Cl_2]$	blue	—	15,150	32	1.82	12, 4
$[Cu(AMEUH)_2]Cl_2$	rose-red	186.6	—	—	1.74	4
$[Cu(AEEUH)_2]Cl_2$	rose-red	216.8	—	—	1.78	4

* Magnetic moments are reported for the corresponding sulphate salt.

acid dissociation constants the 1-amidino-*O*-alkylureas are stronger as co-ordinating agents than amidinourea but somewhat weaker than biguanides.

(d) Mixed chelates of copper(II). Extensive spectrophotometric studies in solution have been completed for the system bis(1-amidino-*O*-alkylurea) copper(II) and orthophenanthroline, 2-2′-dipyridyl, glycine or α-alanine at varied pH in aqueous or aqueous alcoholic medium. Molar ratio variation studies definitely point to 1:1 interaction between the starting copper(II) chelate and one of the above ligands. Convincing spectrophotometric results have been obtained which indicate that the mixed chelates are of the type $[Cu(AAUH)\,(XX/XY)]^{+n}$ (where XX = ophen or dipy and XY = glyH or alan H). The absorption spectra of the mixed chelates[17] Table-3 are suggestive of a distorted octahedral structure for these complexes[19,20]. Atttempts to crystallise the complexes have not as yet succeeded. Similar results have been obtained with the corresponding biguanide complexes and the above chelating ligands, though in the latter case, isolation of the mixed chelates in solid crystalline form has been possible[22].

TABLE 2

INSTABILITY CONSTANTS OF COPPER(II) AND NICKEL(II) COMPLEXES OF 1-AMIDINO-*O*-ALKYLUREAS, AMIDINOUREA AND BIGUANIDES

Ligands	*Instability constants*		*Ref.*
	Copper(II)	*Nickel(II)*	
1-Amidino-*O*-methylurea	1.02×10^{-16}	3.50×10^{-11}	10
1-Amidino-*O*-ethylurea	4.97×10^{-18}	1.55×10^{-12}	10
Amidinourea	6.11×10^{-8}	—	10
Biguanide	4.90×10^{-19}	3.20×10^{-14}	16, 21
N^1-Methylbiguanide	7.08×10^{-18}	1.66×10^{-12}	16, 21
N^1-Ethylbiguanide	1.02×10^{-17}	1.66×10^{-12}	16, 21

TABLE 3

COPPER(II) MIXED CHELATES

System	*Composition*	*pH of maximum formation*	*Electronic spectra*		*Ref.*
			ν, cm^{-1}	*ε*	
[Cu(AMUH)$_2$](Ac)$_2$: dipy	1:1	6–6.5	15,620– 14,710	63	17
[Cu(AMUH)$_2$](Ac)$_2$: ophen	1:1	5.5–6.0	15,870– 14,710	54	17
[Cu(AEUH)$_2$](Ac)$_2$: dipy	1:1	7	15,870– 14,930	64	17
[Cu(AEUH)$_2$](Ac)$_2$: ophen	1:1	5.5–6.0	15,380– 14,710	54	17
[Cu(AMUH)$_2$](Ac)$_2$: glyH	1:1	7	17,540– 16,950	40	17
[Cu(AMUH)$_2$](Ac)$_2$: alanH	1:1	7–8	17,860– 16,950	44	17
[Cu(AEUH)$_2$](Ac)$_2$: glyH	1:1	7	17,540– 16,950	41	17
[Cu(AEUH)$_2$](Ac)$_2$: alanH	1:1	7	17,540– 16,950	44	17

(ii) Nickel(II) complexes

The nickel(II) complexes of these ligands are of the following two types:

(a) Nickel(II) bis(1-amidino-O-alkylurea), [Ni(AAU)$_2$]. These yellow coloured compounds are precipitated from a solution containing nickel(II) ion and excess ligands in the presence of alkali[12]. These have the composition of anhydrobases and are generally insoluble in water but many have been purified by crystallisation from alcohol. The complex nickel base of 1-amidino-*O*-butoxy ethylurea undergoes decomposition when heated with an ammonium salt in aqueous medium.

(b) Nickel(II) bis(1-amidino-O-alkylurea) salts, [Ni(AAUH)$_2$]X$_2$. Treatment of the above complex bases by dilute acids or with ammonium salts lead to the formation of orange-yellow compounds as a consequence of the protonation of the free —NH$_2$ group of the ligands. Starting from the chloride a large number of salts with other anions have been obtained by metathesis. The solubility of the nickel(II) complexes in general is less than that of the corresponding copper(II) complexes. Measurements of electrolytic conductance in aqueous solution or in methanol (for the complexes of 1-amidino-*O*-ethoxyethylurea and butoxyethylurea) provide values in agreement with the bi-univalent nature of the complexes[3,4,13].

The complex nickel bases as well as their salts are diamagnetic. The com-

TABLE 4

NICKEL(II) COMPLEXES OF 1-AMIDINO-*O*-ALKYLUREAS

Compound	*Colour*	*Molar conductance in aqueous solution mhos cm^2 mole^{-1}*	*Electronic spectra*		*Magnetic moment*	*Ref.*
			ν, cm^{-1}	*ε*		
$[Ni(AMUH)_2]Cl_2$	yellow	251.0	22,730	55	diamagn.	10, 13
$[Ni(AEUH)_2]Cl_2 \cdot 2H_2O$	yellow	247.8	22,730	47	diamagn.	10, 13
$[Ni(AMEUH)_2]Cl_2$	yellow	218.6	22,220	45	diamagn.	4
$[Ni(AEEUH)_2]Cl_2$	yellow	161.5*	22,220	46	diamagn.	4

* In methanol solution.

plexes show bands around 22,730–22,220 cm^{-1} in their electronic spectrum[4,10]. The electronic spectra* and the diamagnetism are regarded as diagnostic of a square planar arrangement[23–25], (Table 4).

The formation of some of these nickel(II) complexes namely of 1-amidino-*O*-methylurea and 1-amidino-*O*-ethylurea has been followed quantitatively by spectral measurements. These studies show that unlike the copper(II) complexes the nickel(II) bis(1-amidino-*O*-alkylurea) complexes are formed in a single step. The instability constants have been evaluated and these are slightly lower than those of biguanide complexes[10,21,16].

(iii) Cobalt(II) complexes

The 1-amidino-*O*-alkylureas react with cobalt(II) salts in the presence of ammonia to precipitate cream coloured bis(1-amidino-*O*-alkylurea) cobalt(II)[26]. Whereas the biguanide sulphate and cobalt(II) salts react under similar conditions to precipitate bis(biguanide) cobalt(II) sulphate[27] or, in the presence of NaOH, the bis(biguanide) cobalt(II) hydroxide, the 1-amidino-*O*-alkylureas provide the cobalt(II) complexes as the anhydrobases. The magnetic moments of several cobalt(II) complexes all lie within the range 2.3–2.5 B.M. Since the complexes are all anhydrobases, these measurements appear to indicate a square planar structure. In acetone solution the complexes remain pale yellow and spectral measurements indicate absence of any band in the tetrahedral cobalt(II) region (650–700 mμ)[28,29,30] and also of any band in the octahedral cobalt(II) region (~550 mμ)[31,32,33]. A planar quadrico-ordinate complex of cobalt(II) should show a band around 1200 mμ[34,35]. But unfortunately this region has not been covered in the above study.

The above complexes are, however, more susceptible to donor solvents. Thus in methanol, tetrahydrofuran and also in dioxan, rapid oxidation occurs

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* Note added in proof: A detailed study of the absorbtion spectra of several nickel (II) complexes in the solid state and in different solvents has since appeared. V. RASMUSSEN AND W. A. BAKER, *J. Chem. Soc. A*, (1967) 580.

TABLE 5

COBALT(II) COMPLEXES OF 1-AMIDINO-*O*-ALKYLUREAS

Compound	*Colour*	*Molar conductance in methanol mhos cm^2 mole^{-1}*	*Magnetic moment (B.M.)*	*Ref.*
[Co(AMU)$_2$]	dirty yellow silky crystals	21	2.34	26
[Co(AEU)$_2$]	pale yellow	11	2.36	26
[Co(AP^{i}U)$_2$]	pale yellow	21	2.52	26
[Co(AB^{n}U)$_2$]	pale yellow	20	2.36	26
[Co(AB^{i}U)$_2$]	pale yellow	21	2.32	26
[Co(AA^{i}U)$_2$]	pale yellow	20	2.52	26

with the appearance of the two usual cobalt(III) bands[36,37] around 330–350 mμ and 480–500 mμ.

These complexes liberate ammonia from ammonium salts and undergo ready oxidation to cobalt(III). However, they are quite stable in the dry solid state even at 120 °C, (cee Table 5).

(iv) Cobalt(III) complexes

Cobalt(III) complexes are of the following types:

(a) Tris-1-amidino-O-alkylurea cobalt(III)-complexes, [Co(AAUH)$_3$]X_3 *and hetero 1-amidino-O-alkylurea cobalt(III) complexes.* The hydrated bases of these chelates have been obtained by oxidising a mixture of cobalt(II) salts and an excess of the ligands[38,39] concerned by H_2O_2. These are generally dark-red in colour and their solubility in aqueous solution decreases with increase in the chain length of the substituent, whereas that in ethanol and acetone increases. The complexes liberate ammonia from ammonium salts and form the corresponding salts. Conductance measurements in aqueous solution indicate the tri-univalent electrolytic nature of the complexes. The electronic absorption spectra reveal the usual two bands of octahedral cobalt(III) chelates around 28,000 and 21,000 cm^{-1} representing the two transitions $^1T_{2g} \leftarrow {}^1A_{1g}$ and $^1T_{1g} \leftarrow {}^1A_{1g}$. The compounds are all diamagnetic. Although corresponding biguanide complexes are resolvable into optical isomers, these chelates could not be resolved presumably due to their high solubility in aqueous medium.

A hetero 1-amidino-*O*-ethylurea bis(1-amidino-*O*-methylurea) has also been obtained by the action of 1-amidino-*O*-ethylurea on the diammine bis(1-amidino-*O*-methylurea) cobalt(III) complex. The complex is highly soluble, behaves as a tri-univalent electrolyte and exhibits two ligand field bands[39] at 27,800 cm^{-1} and at 20,800 cm^{-1}.

(b) Bis(1-amidino-O-alkylurea) cobalt(III) complexes. The complexes belonging to this category can be sub classified as follows:

(1) $[Co(AAUH)_2X_2]^{+n}$ where X = NH_3, Py, β-picoline, CH_3CN

(2) $[Co(AAUH)_2X_2]^{+1}$ where X = NO_2 or CN

(3) $[Co(AAUH)_2(AA)]^{+n}$ where AA = ophen, dipy, glyH, en, bigH.

(1) $[Co(AAUH)_2X_2]^{+n}$. Air oxidation of a mixture of cobalt(II) salts, 1-amidino-*O*-alkylurea sulphate (1:2) in the presence of ammonia leads to the syntheses of diammine bis (1-amidino-*O*-alkylurea) cobalt(III) complexes. The 1-amidino-*O*-alkylurea ligands undergo protonation to different extents depending on the experimental conditions of the syntheses. Thus monopositive $[Co(NH_3)_2(AMU)_2]^+$, bipositive $[Co(NH_3)_2(AMU)(AMUH)]^{2+}$ and tripositive $[Co(NH_3)_2(AMUH)_2]^{3+}$ have all been isolated in the form of a large number of salts[40]. Extensive measurements of the equivalent weights and conductance in aqueous solution have been reported in order to confirm the ionic natures of the different complex species. Oxidation of the freshly prepared yellow coloured bis(1-amidino-*O*-alkylurea) cobalt(II) in the presence of ammonia also leads to many similar products. The yellow *bis* complex readily liberates ammonia from aqueous ammonium thiocyanate solution providing crystals of $[Co(NH_3)_2(AAU)(AAUH)](SCN)_2$. Failure of such a reaction with KSCN indicates that the reaction with ammonium thiocyanate first leads to the release of ammonia in solution which then forms the diammine complex, the whole process being favoured by the presence of the thiocyanate ion[40].

The above diammine complex reacts with oxalic acid at room temperature to provide rose-red $[Co(NH_3)_2(AAUH)_2](C_2O_4)_{1.5}$ and on a steam bath the intense violet oxalato–oxalate salt $[Co(C_2O_4)(AAUH)_2](C_2O_4)_{0.5}$. The reactions with other bidentate ligands (*e.g.* *o*-phen, dipy, glyH, en or BigH) to produce the heterochelates $[Co(ophen)(AAUH)_2]^{+3}$ etc. do not proceed below 65–70 °C. These reactions have been taken to suggest tentatively a *trans* diammine structure for these complexes. A comparison with the reactions of *cis* and *trans* diammine-bis(biguanide) cobalt(III) salts[41,42] appears to support such a *trans* configuration for the above complexes.

Hydrogen peroxide oxidation of the cobalt(II) complex in the presence of ammonia was also undertaken and a diamminebis(1-amidino-*O*-alkylurea) isolated. The visible absorption spectra of this product as also the one obtained by an air oxidation method were identical, both showing absorption bands at 330–340 mμ and at 486–505 mμ. The expected further splitting[43,44] of the lower energy absorption bands due to a tetragonal field was not realised due to the close positions of ammonia and the 1-amidino-*O*-alkylureas in the spectrochemical series. Splitting of the first visible absorption spectral band has been observed in *trans* (dihalogenoacetato) (tetrammine) cobalt(III)[45] and diacetato bis (ethylenediamine) cobalt(III)[46] and similar complexes[47] though not in the cases of *cis* and *trans* isomers of diamminebis(ethylenediamine) cobalt(III)[48].

Replacement of ammonia by pyridine during the air oxidation of the cobalt(II) complex has provided a series of variedly protonated cations *viz.* $[Co(Py)_2(AMU)_2]^I$ and $[Co(Py)_2(AMUH)_2]^{I_3}$. Equivalent weight and conductance studies have been made to elucidate the ionic nature of these complexes[49]. The reactions of oxalic acid and other bidentate ligands with these complexes have been studied with results similar to those for the diammine series. The electronic absorption spectra show the usual two ligand field bands around 29,000 cm^{-1} and 20,000 cm^{-1}. Similar complexes with β-picoline and acetonitrile have also been characterised[49]. The complexes are believed to possess *trans* disposition of the two unidentate ligands, (Table 6).

(2) $[Co(AAUH)_2X_2]^+$ where $X = NO_2$ or CN. Two series of dinitrobis (1-amidino-*O*-alkylurea) cobalt(III) nitrite have been synthesised and characterised. Aerial oxidation of cobalt(II) nitrate, 1-amidino-*O*-alkylurea sulphate and sodium nitrite in aqueous solution provides orange red crystals of the *trans* derivative. Action of 1-amidino-*O*-alkylurea sulphate on sodium cobaltinitrite on the other hand leads to the brownish red *cis* dinitro series[50]. Evidence has been cited in favour of the *cis-trans* isomerisation. The salts of the *cis* series provide much lower conductance values in methanol (Λ_M = 37–55 mhos) in contrast to the normal conductivity (Λ_M = 100–105 mhos) of the *trans* series. The low conductance of the *cis* complexes has been interpreted to arise out of strong ion-pair formation[51–52]. The electronic absorption spectra of both the series show two similar bands around 350 mμ ($^1T_{2g} \leftarrow {}^1A_{1g}$ transition) and around 440–480 mμ ($^1T_{1g} \leftarrow {}^1A_{1g}$ transition). The *cis* complexes, however, provide distinctly higher molar absorptivity. The infra-red absorption spectra do not show any band around 1050 cm^{-1} indicating the absence of a metal oxygen linkage arising from a nitrito complex. Both the samples, however, show strong bands around 810–830 cm^{-1} due to bending modes of the nitrite group. The *trans* compound, however, gives only one band at 1315 cm^{-1}, whereas the brown-red *cis* variety shows as expected, two bands[53] at 1310 cm^{-1} and at 1335 cm^{-1}. The *cis* series of salts has a slightly higher solubility in methanol than the corresponding *trans* series. Both series of complexes are stable to heat at 120 °C and on boiling in aqueous medium there occurs no evolution of nitrous fumes. On treatment with dilute HCl, however, nitrous fumes evolve and reduction to cobalt(II) takes place[50].

The action of KCN on tris (1-amidino-*O*-methylurea) cobalt(II) base or on tris (1-amidino-*O*-ethylurea) cobalt(III) base and also on diamminebis (1-amidino-*O*-alkylureas) has led to the isolation of dicyanobis(1-amidino-*O*-alkylurea) cobalt (III) base as yellow coloured products. These are highly soluble in aqueous medium. A *trans* configuration has been assumed[40]. A *trans* configuration earlier proposed intuitively for the dicyanobis (biguanido) cobalt(III) has recently been confirmed in our Laboratory from an infra-red study[55].

(3) $[Co(AAUH)_2(AA)]^{+n}$ where AA = ophen, dipy, glyH, en and bigH. A series of heterochelates cobalt(III) complexes has been obtained by the action of bidentate ligands such as *ortho*phenanthroline, 2-2′-dipyridyl, ethylenediamine etc. on diaminine bis (1-amidino-*O*-alkylurea) cobalt(III) or on dipyridinebis (1-amidino-*O*-alkylurea) cobalt(III) complexes. The resulting heterochelate complexes are highly soluble in aqueous solution. All these exhibit the usual cobalt(III) spectral bands, the position of the bands being in conformity with the established sequence of these ligands in the spectrochemical series[56, 57].

The heterochelates, biguanidebis(1-amidino-*O*-alkylurea) cobalt(III) complexes have reasonable solubility and have been described in the form of a number of salts[39]. Conductance and equivalent weight measurements identify the compounds as tri-univalent electrolytes. The two ligand field bands are observed around 28,000 cm^{-1} and 21,000 cm^{-1}. The 1-amidino-*O*-methylurea and 1-amidino-*O*-ethylurea heterochelates have been resolved by the fractional crystallisation of the *d*-camphor-10-sulphonate salts. The pure levo diastereoisomer has been reported. The corresponding dextro diastereoisomer was obtained in poor yield and low purity. Treatment of the levo disastereoisomer with potassium iodide provided the iodide salt of the levo cation[39].

(c) *1-amidino-O-alkylureabis(biguanide)cobalt(III) complexes.* Action of 1-amidino-*O*-alkylureas on *cis* diamminebis (biguanide) cobalt(III) has given rise to a series of highly crystalline and moderately soluble red coloured complexes of 1-amidino-*O*-alkylureabis(biguanide) cobalt(III)[57]. A large number of salts are known with tri-univalent electrolytic nature. The electronic absorption spectral measurements reveal two ligand field bands around 28,500 cm^{-1} and 21,000 cm^{-1}. A number of these cations have been resolved *via* fractional crystallisation of the chloride dextrotartrate and the dextro camphorsulphonate salts. Addition of the chloride salt to an excess of sodium dextrotartrate provides, on cooling, crystals which are very rich in the levo diastereoisomer. Further fractionation of these crystals provides the pure diastereoisomer which has been converted to the *levo* sulphate. On the other hand, the *dextro*camphorsulphonate salt appears in the racemic form from which fractional crystallisation provides both the diastereoisomers. In both these cases the *levo* diastereoisomer forms the less soluble fraction. However, attempts to obtain the iodide salt from the camphorsulphonate led to substantial loss of optical activity, (Table 7).

Replacement of a biguanide molecule of tris (biguanide) cobalt(III) complex by any of the several 1-amidino-*O*-alkylureas does not change the sign of rotation of the less soluble diastereoisomer. Replacement of a biguanide by 1-amidino-*O*-alkylurea introduces a greater asymmetry as is revealed by higher molar rotation values. Furthermore among the 1-amidino-*O*-alkylureas themselves, asymmetry appears to decrease with increasing chain length of the alkyl substituent.

Both the diastereoisomers and the pure active complex sulphates are per-

TABLE 6

COBALT(III) COMPLEXES OF 1-AMIDINO-*O*-ALKYLUREAS

Compound	*Colour*	*Molar conductance mhos cm² mole⁻¹ (in water)*	*Electronic spectra*				*Ref.*
			Band II		*Band I*		
			ν, cm⁻¹	*ε*	*ν, cm⁻¹*	*ε*	
$[Co(NH_3)_2(AMU)]Cl \cdot 2.5H_2O$	rose-red	144.7	30,000	630	20,400– 20,000	70	40
$[Co(NH_3)_2(AMU)(AMUH)]SO_4$	rose-red	324.0	30,000	450	20,000– 19,600	85	40
$[Co(NH_3)_2(AEUH)_2]I_3 \cdot 2H_2O$	orange	450.9	33,000– 30,000	330	20,600– 19,800	102	40
$[Co(Py)_2(AEUH)_2](NO_3)_3$	rose-red	501.9	29,000– 28,600	280	20,400– 20,000	93	49
cis$[Co(NO_2)_2(AA^iUH)_2]NO_2$	brownish-red	55.0	30,000	5640	22,700– 21,700	416	50
trans$[Co(NO_2)_2(AA^iUH)_2]NO_2$	orange	91.7	30,000	5560	21,700– 21,300	376	50
$[Co(ophen)(AMUH)_2]Cl_3 \cdot 6H_2O$	rose-red	458.4	30,000	1600	21,300– 21,000	146	56
$[Co(dipy)(AMUH)_2]Cl_3 \cdot 7H_2O$	rose-red	438.3	30,000	1530	21,300– 21,000	176	56
$[Co(gly)(AMUH)_2]I_2$	brownish-red	285.8*	28,600– 28,200	214	19,800	131	56
$[Co(en)(AMUH)_2](SO_4)_{1.5} \cdot 5H_2O$	orange	462.0*	28,600– 28,200	132	20,800	160	56
$[Co(BigH)(AMUH)_2]I_3$	orange	467.4	28,600	219	20,300	229	39
$[Co(AEUH)(AMUH)_2]I_3 \cdot H_2O$	orange	472.2	27,800– 27,400	330	20,800– 20,600	234	39
$[Co(AEUH)(BigH)_2]Cl_3 \cdot 5H_2O$	orange-yellow	445	28,100	210	21,100	225	58
$[Co(AP^iUH)_3](SO_4)_{1.5} \cdot 2.5H_2O$	rose-red	391.2*	29,000– 27,800	192	21,000– 20,600	180	56

* Molar conductance for the corresponding chloride salts.

TABLE 7

CHARACTERISTICS OF THE OPTICAL ISOMERS OF COBALT(III) COMPLEXES OF 1-AMIDINO-*O*-ALKYLUREAS

Compound	$[\alpha]_D^t$, *degrees*	$[M]_D^{t*}$, *degrees*	*Ref.*
$l[\mathrm{Co(BigH)\,(AMUH)_2](CS)_3}$	−200	−2174	39
$l[\mathrm{Co(BigH)\,(AMUH)_2]I_3}$	−250	−1930	39
$l[\mathrm{Co(AMUH)\,(BigH)_2]^{Cl}{}_{d\text{-}tart} \cdot 4.5H_2O}$	−375	−2396	57
$l[\mathrm{Co(AMUH)\,(BigH)_2](SO_4)_{1.5} \cdot 3H_2O}$	−408	−2338	57
$l[\mathrm{Co(AEUH)\,(BigH)_2]^{Cl}{}_{d\text{-}tart} \cdot 4.5H_2O}$	−337	−2197	58
$l[\mathrm{Co(AEUH)\,(BigH)_2](SO_4)_{1.5} \cdot 3H_2O}$	−375	−2197	58
$l[\mathrm{Co(AP^iUH)\,(BigH)_2]^{Cl}{}_{d\text{-}tart} \cdot 4H_2O}$	−325	−2139	57
$l[\mathrm{Co(AP^iUH)\,(BigH)_2](SO_4)_{1.5} \cdot 3H_2O}$	−350	−2104	57
$l[\mathrm{Co(AB^iUH)\,(BigH)_2]^{Cl}{}_{d\text{-}tart} \cdot 4.5H_2O}$	−325	−2213	57
$l[\mathrm{Co(AB^iUH)\,(BigH)_2](SO_4)_{1.5} \cdot 2H_2O}$	−350	−2090	57

* $[M]_D^t = \dfrac{[\alpha]_D^t \times \text{Molecular weight}}{100}$

fectly stable in aqueous solution at 25 °C. There was no evidence of racemization taking place when the products were heated up to 120 °C for several hours. These optical isomers are interesting materials both from the point of view of mechanistic studies of racemization as well as being suitable molecules for study by the techniques of optical rotatory dispersion and circular dichroism.

(v) Oxo-vanadium(IV) complexes

A few oxovanadium(IV) complexes[59] of 1-amidino-*O*-alkylureas and 1-amidino-*O*-alkoxyalkylureas have been prepared by the action of alkali on a mixture of vanadylsulphate and a large excess of the ligands. These form bluish green to rose-violet crystals and conform to anhydrobase formula. They have magnetic moment values of about 1.7 B.M. indicative of quadrivalent vanadium, and resemble the oxo-vanadium(IV) complexes of biguanides and some substituted biguanides[60]. The complexes are insoluble in common solvents. The electronic absorption spectra and infra-red spectra have not been recorded, (see Table 8).

(vi) Palladium(II) complexes

Complex palladium(II) bis (1-amidino-*O*-alkylurea) sulphates have been prepared as sparingly soluble products by the addition of sodium chloropalladite to that of the 1-amidino-*O*-alkylurea sulphate in faintly ammoniacal medium[3,4,61]. The chloride and a few other salts have also been reported. The complex bases react with ammonium salts to liberate ammonia providing the corresponding salts.

The thiocyanate salts on treatment with dilute acid solution and on warming provide insoluble, ruby-red coloured palladium(II) bis (1-amidino-*O*-alkylurea) palladothiocyanates.

$$2\,[\mathrm{Pd(AAUH)^2}]\,(\mathrm{SCN})_2 + 2\,\mathrm{HCl} \rightarrow [\mathrm{Pd(AAUH)_2}]\,[\mathrm{Pd(SCN)_4}]_- + 2\,\mathrm{AAUH.HCl}$$

The complexes are all stable to boiling water and alcohol, provide the expected conductance values and like the corresponding nickel(II) complexes, are diamagnetic pointing to square planar stereochemistry, (Table 8).

TABLE 8

OXO-VANADIUM(IV) AND PALLADIUM(II) COMPLEXES OF 1-AMIDINO-O-ALKYLUREAS

Compound	*Colour*	*Magnetic moment (B.M.)*	*Molar conductance mhos cm^2 mole^{-1}*	*Ref.*
$[\mathrm{VO(AMU)_2}]$	bluish green	1.67	—	59
$[\mathrm{VO(AEU)_2}]$	bluish green	1.68	—	59
$[\mathrm{VO(AEEUH)_2}]$	sky blue	1.67	—	59
$[\mathrm{VO(AB^nEU)_2}]$	light grey-violet	1.69	—	59
$[\mathrm{Pd(AMUH)_2]Cl_2 \cdot 2H_2O}$	cream	diamagnetic	171.2	61
$[\mathrm{Pd(AEUH)_2]Cl_2 \cdot 2.5H_2O}$	cream	diamagnetic	224.8	61
$[\mathrm{Pd(AB^nUH)_2]SO_4 \cdot 2H_2O}$	cream	diamagnetic	—	4
$[\mathrm{Pd(AMEU)_2}]$	cream	diamagnetic	—	4
$[\mathrm{Pd(AEEU)_2}]$	cream	diamagnetic	—	4
$[\mathrm{Pd(AB^nU)_2}]$	cream	diamagnetic	—	4

(vii) Zinc(II) complexes

Zinc(II) forms colourless crystalline materials having the formula $[\mathrm{Zn(AAU)_2}]$. The complex bases are very weak, being more or less hydrolysed in water and do not form any salts[62].

(viii) Chromium(III) complexes

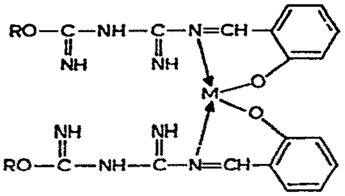
Chromium(III) complexes[63] have been isolated as rose-red anhydrobases having the formula $[\mathrm{Cr(AAU)_3}]\mathrm{X\ H_2O}$ by the addition of a chrom-alum solution to an alkaline solution of 1-amidino-O-alkylurea sulphates. On treating the complex bases with dilute H_2SO_4, the complex sulphates were obtained as orange red precipitates. The chromium(III) complexes are less stable than the cobalt(III) complexes. The studies so far reported on chromium(III) are admittedly very sketchy and call for further investigation.

(ix) Boron(III) complexes

1-Amidino-O-alkylureas react with trimethoxy borate in methanol to give crystalline[64] compounds $[\mathrm{B(AAU)\,(OCH_3)_2}]$. These hydrolyse in aqueous solution and rapidly in acid solution, melt around 400 °C and decompose explosively in air. It is to be hoped that further studies will soon be reported on these complexes.

D. REACTIONS OF CO-ORDINATED 1-AMIDINO-*O*-ALKYLUREAS

Copper(II) bis (1-amidino-*O*-alkylurea) base and the corresponding nickel(II) complex were found to react readily with salicylaldehyde on refluxing to provide complexes of the following types[65].

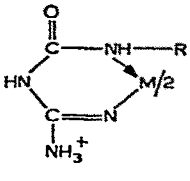


where M = Cu^{II}, Ni^{II}, Co^{II} and R = CH_3, C_2H_5, n-C_3H_7, iso-C_3H_7, n-C_4H_9 and iso-C_4H_9

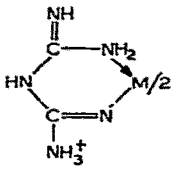
The tris (1-amidino-*O*-alkylurea) cobalt(III) base apparently underwent a similar reaction but yielded a cobalt(II) complex. The copper(II) complexes are green to brown and have magnetic moment values around 1.85–1.97 B.M. The absorption spectra have not been reported and therefore no definite conclusion can be drawn about the stereochemistry. The nickel(II) complexes of methyl, ethyl, *n*-propyl or isopropyl derivatives with salicylaldehyde ($NiL_2.2H_2O$, where LH = ligand) are green to greenish yellow and magnetic moments have been regarded as indicative of octahedral nickel(II). However with *n*-butyl and isobutyl substitution, the nickel(II) complexes are orange red and diamagnetic. The authors believe that steric influence of the bulky substituents results in square planar structure. The brown coloured cobalt(II) complexes with magnetic moment values 3.2–3.6 B.M. are stated to be of tetrahedral stereochemistry. However, these values are much below the tetrahedral range (4.3–4.7) and no spectral confirmation or otherwise of the stereochemistry is presently available.

E. STRUCTURE OF METAL CHELATES

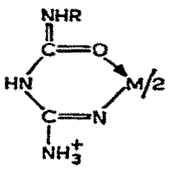
Originally the chelated structure (I) was suggested[12] in keeping with the structure of metal biguanide complexes (II). An alternate structure (III) was discarded by the authors on the ground that copper offers green coloured complexes with acyloin oxime in which it is linked with both nitrogen and oxygen atoms of the ligand, whereas the copper derivatives of the present ligands are all rose-red



I



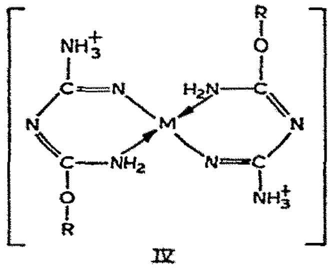
II



III

in colour. Moreover in a molecule of these ligands oxygen was considered unlikely to be available for co-ordination with the metal due to the possible formation of hydrogen bonds[12].

Since the nature of these ligands is now extensively investigated and properly named as 1-amidino-*O*-alkylureas instead of 1-amidino-3-alkylureas or guanylalkylureas, their metallic complexes may be represented by structure (IV)[6,8].



IV

The presence of free amino groups in these chelates has been demonstrated by their reaction with salicylaldehyde to provide complex of amidino-*O*-alkylurea Schiff base type ligands as already mentioned in section D.

F. CONCLUDING REMARKS

The studies so far reported have established the strong field character of these fascinating ligands, which follow closely the biguanides and substituted biguanides in their transition metal chemistry. It is to be hoped that extensive studies will be undertaken in future years to explore the donor properties of these ligands to a still greater extent.

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