Complexes of *N*-Hydroxyethylethylenediamine and Its Condensation Product with Acetone

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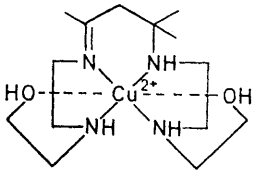
The preparation of a number of 1 : 3, 1 : 2, and 1 : 1 complexes of *N*-hydroxyethylethylenediamine with cobalt(II), nickel(II), copper(II), and zinc(II) salts is described and their structures are discussed. The co-ordinated ligand reacts readily with acetone *via* condensation with the primary amino-group to give complexes of 7,9,9-trimethyl-3,6,10,13-tetra-azapentadeca-6-en-1,15-diol. These are reported for copper(II) halides and nickel(II) bromide. Attempts to prepare a similar complex with zinc(II) chloride lead to the formation of a 1 : 1 species, Zn(hen + acetone − H_2O)Cl_2. Acetone and *N*-hydroxyethylethylenediamine also condense readily in the absence of metal ion, but attempts to form complexes of this product with a number of metal salts led only to the formation of previously characterised complexes of *N*-hydroxyethylethylenediamine.

THERE have been several studies of the metal complexes formed by *N*-hydroxyethylethylenediamine (hen) both in solution [1] and in the solid state. Breckenridge [2] reported the formation of Cu(hen)$_2X_2$ (X = Cl or Br), Ni(hen)$_3Cl_2$, and Cu(hen)Cl_2,$2H_2O$, while Das Sarma and Bailar [3] have shown that the molecule may act as a bidentate or terdentate ligand. In the first case the ligand co-ordinates through the amino-nitrogen atoms, while the OH group may co-ordinate as such, or depending upon the presence of suitable bases, as a deprotonated group. They were unable to prepare tris-complexes.


(1)

Patel and Curtis [4] have shown that the amino-group of hen in Cu(hen)$_2$(NO_3)$_2$ will condense with acetone eventually giving a complex with a linear hexadentate ligand (I). They were unable to prepare a similar product starting from Ni(hen)$_3$(ClO_4)$_2$. We have prepared a number of complexes of hen and have attempted to examine the role of the metal ion in the condensation of the ligand with acetone.

EXPERIMENTAL

In general the complexes were prepared by adding the ligand dropwise, with stirring, to a solution of the metal salt in hot absolute ethanol. The complexes precipitated readily, and were filtered off and washed with ethanol and light petroleum ether. Preparations with metal salt and ligand in 1 : 1 and 1 : 2 molar ratios gave 1 : 1 and 1 : 2 complexes, but in general apart from [Ni(hen)$_3$]X_2 (X = Cl, Br), only 1 : 2 complexes could be obtained from preparations with higher concentrations of ligand. Analytical data are presented in Table 1.

The complexes with the condensed ligand–acetone molecule were prepared either by refluxing 1 : 2 complexes in acetone for periods of up to 2 h, or by dissolving the metal

[1] R. C. Courtney, R. L. Gustafson, S. Chaberek, and A. E. Martell, *J. Amer. Chem. Soc.*, 1959, **81**, 519; R. Nasanen, P. Tilus, and A.-M. Rinne, *Suomen Kem.*, 1966, **39**, 45.

[2] J. G. Breckenridge, *Canad. J. Res.*, 1948, **26B**, 11.

[3] B. Das Sarma and J. C. Bailar, jun., *J. Amer. Chem. Soc.*, 1969, **91**, 5958.

[4] V. C. Patel and N. F. Curtis, *J. Chem. Soc. (A)*, 1969, 1607.

salt in acetone, adding a six-fold excess of ligand and refluxing. With $NiBr_2$ a light blue precipitate was formed first. This redissolved eventually giving a pink precipitate after refluxing for 1 h. With $CuBr_2$ a green precipitate was initially formed which turned blue-mauve on refluxing for 2 h. The products were filtered off, washed with acetone and ether, and dried *in vacuo*. Both methods gave identical products, and it is clear that in the second method a complex of hen is first formed before condensation with acetone occurs.

The condensation of ligand and acetone in the absence of metal ions was effected by adding an excess of dried acetone to the ligand (a considerable amount of heat was evolved, with a temperature rise of 20°) and refluxing for 30 min. The excess acetone was distilled off leaving an amber coloured liquid with an analysis corresponding to (hen + acetone − H_2O). The i.r. spectrum showed a band at 1654 cm^{-1} ($\nu_{C=N}$) and confirmed the loss of C=O and NH_2 groups. The presence of traces of diacetone alcohol was indicated by the n.m.r. spectrum. Attempts were made to prepare complexes of the condensed species by adding different excesses to acetone or alcohol solutions of metal salts and warming. Only complexes of hen were formed. No product was obtained showing an absorption at *ca.* 1660 cm^{-1} in the i.r. spectrum.

I.r. spectra were measured as Nujol and HCB mulls on Perkin-Elmer 237 and Grubb–Parsons DM4 instruments using sodium chloride and Polythene supports respectively. Reflectance spectra were measured on a Unicam SP 700 spectrophotometer, magnetic moments on a Gouy balance, and conductivities on a Doran bridge for 10^{-3}M-aqueous solutions. The complexes were insoluble in other solvents examined. Molecular weights were measured on a Hewlett–Packard Vapour Pressure Osmometer, calibrated with benzil.

RESULTS AND DISCUSSION

The co-ordination behaviour of *N*-hydroxyethylethylenediamine is readily followed by i.r. spectroscopy.[3,5] The presence of a non-co-ordinated hydroxyethyl group is shown by the presence of a band, assignable to free ν_{OH} at *ca.* 3380 cm^{-1}. The band in the free ligand is lowered by hydrogen bonding, and by co-ordination when the ligand is terdentate. Magnetic moments and conductivities are given in Table 1, and spectroscopic data in Table 2.

(a) 1 : 3 *Complexes*. Despite considerable effort only $[Ni(hen)_3]X_2$ (X = Cl, Br) could be prepared. These are 2 : 1 electrolytes while the electronic spectra of the compounds are identical, confirming ionic halide. The spectra may be assigned in O_h symmetry. The magnetic moments are consistent with such a structure. Here, obviously, the ligand is bidentate. This is confirmed by the presence of strong bands at 3380 cm^{-1} in their i.r. spectra. The value of Δ_0 for the ligand co-ordinated *via* two nitrogen donors is 10·8 kK. This compares with Δ_0 = 11·5 kK for ethylenediamine. The lower value for *N*-hydroxyethylethylenediamine may result from a steric effect of the CH_2CH_2OH group.

(b) 1 : 2 *Complexes*. The following have been prepared: $[Ni(hen)_2]X_2$ (X = Br, NO_3, ClO_4), $[Cu(hen)_2]X_2$ (X = Cl, Br, NO_3, ClO_4), $[Cu(hen)_2](NO_3)_2,H_2O$, and $[Zn(hen)_2]Br_2$. The $[Cu(hen)_2]X_2$ complexes have been briefly reported.[2,4] We have prepared two forms of $[Ni(hen)_2]X_2$ (X = Br, ClO_4), characterised by different electronic spectra. Some preparations gave a product [denoted by (A)] having an electronic spectrum identical to that of $[Ni(hen)_2](NO_3)_2$ and characteristic of a tetragonally distorted nickel(II) complex with the lowest energy band split. In other cases the product (B) had a spectrum in which the highest energy band was lowered by some 5 kK compared with that of (A). On standing for some weeks, type (B) rearranged to give type (A) identical to that prepared directly. We were unable to prepare type (B) $[Ni(hen)_2](NO_3)_2$. The spectrum of (B) does not appear to be that of an octahedral species. It may be a mixture of (A) and a second product of co-ordination number 5 with trigonal bipyramidal stereochemistry.[6] For the terdentate ligand Δ_0 = 10·3 kK, a value which is in accord with the relative donor strengths of OH and amine groups.

All the 1 : 2 complexes are 2 : 1 electrolytes, as confirmed in the appropriate cases by their i.r. spectra which indicated that the oxy-anions were not co-ordinated. With one exception the spectra also showed that the hydroxy-group was co-ordinated. The copper and zinc complexes must be six-co-ordinate, therefore, with terdentate ligand. The exception is $[Cu(hen)_2](ClO_4)_2$ where it is clear that the OH group is free. We have therefore assigned a square planar structure to this complex. Magnetic moments and electronic spectra are consistent with these structures.

(c) 1 : 1 *Complexes*. These include $[Ni(hen)H_2O]X_2$ (X = Cl, Br), $[Co(hen)H_2O]X_2$ (X = Cl, Br, NCS) together with the deaquated species; $Cu(hen)(NO_3)_2$; $Cu(hen)Cl_2$ and $Zn(hen\text{-}H^+)Br$.

The electronic spectra of the nickel aquo-complexes show them to have a distorted octahedral structure, and also indicate that the halide ions are not co-ordinated. They undergo aquation in aqueous solution. On careful heating *in vacuo* one mole of water is lost, with correct weight loss, giving $Ni(hen)X_2$ (X = Cl, Br). The loss of water is confirmed by their i.r. spectra. A colour change also occurs, while the electronic spectra in addition to showing the maintenance of the octahedral stereochemistry, show that the halide is co-ordinated, the bands in the spectrum of the chloro-complex being at higher energy than those of the bromo-complex. It is difficult to formulate structures for these complexes. In the case of the aquo-*N*-hydroxyethylethylenediaminenickel(II) cation the structure must be polymeric. A possible structure is one with in-plane bridging hydroxy- and aquo-groups, with the $NH_2CH_2CH_2NH^-$ portion of the ligand bridging axial positions. Studies with models indicates that this co-ordination mode is possible. The postulation of bridging hydroxy- and aquo-groups is not usual. The structures of the halogeno-complexes may be more readily understood, particularly if both halide ions are co-ordinated. Possibly however the

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[5] J. A. Broomhead, *J. Amer. Chem. Soc.*, 1968, **90**, 4480.

[6] M. Ciampolini and N. Naidi, *Inorg. Chem.*, 1966, **5**, 41.

TABLE 1

Analytical data, magnetic moments, and conductivities

Complex	Colour	Calculated %			Found %			μ_{eff} (B.M.)	Conductivities Ω^{-1} cm^2 mol^{-1}
		C	H	N	C	H	N		
$\mathrm{Ni(hen)_3Cl_2}$	Blue-mauve	32·6	8·15	19·0	32·1	8·0	18·3	3·01	196
* $\mathrm{Ni(hen)_3Br_2}$	Blue-mauve	27·1	6·75	15·8	26·7	6·65	15·8	3·01	230
* $\mathrm{Ni(hen)_2Br_2(A)}$	Blue	22·45	5·65	13·1	22·65	5·75	12·95	3·13	270
* $\mathrm{Ni(hen)_2(NO_3)_2}$	Blue	24·4	6·15	21·5	24·3	6·15	21·0	3·07	197
* $\mathrm{Ni(hen)_2(ClO_4)_2(B)}$	Blue	20·6	5·15	11·8	21·2	5·1	11·8		232
* $\mathrm{Ni(hen)Cl_2H_2O}$ [a]	Light green	19·1	5·55	11·15	18·8	5·6	10·85	3·18	235
* $\mathrm{Ni(hen)Br_2H_2O}$	Light green	14·1	4·1	8·22	14·2	4·3	8·25	3·18	
$\mathrm{Cu(hen)_2Cl_2}$ [b]	Blue	28·05	7·05	16·35	27·2	7·0	16·4	1·87	250
$\mathrm{Cu(hen)_2Br_2}$ [c]	Blue	22·25	5·55	13·0	21·6	5·3	12·5	1·84	240
* $\mathrm{Cu(hen)_2(NO_3)_2}$	Blue	24·3	6·05	21·2	24·0	5·95	21·0	1·82	
$\mathrm{Cu(hen)_2(NO_3)_2H_2O}$	Blue	23·2	6·3	20·35	23·05	5·7	20·1	1·91	243
$\mathrm{Cu(hen)_2(ClO_4)_2}$	Blue	20·4	5·1	11·9	20·55	5·8	11·95	1·96	240
* $\mathrm{Cu(hen)(NO_3)_2}$ [d]	Blue	16·45	4·2	19·2	16·2	4·0	18·4	1·87	242
$\mathrm{Cu(hen)Cl_2}$	Light green	20·2	5·05	11·75	20·4	5·15	11·75	1·93	246
* $\mathrm{Co(hen)Cl_2}$	Dark blue	20·55	5·15	12·0	21·1	5·2	11·6	(3·85)	
* $\mathrm{Co(hen)Br_2}$	Dark green	14·95	3·7	8·65	16·5	3·8	9·15	(3·61)	
* $\mathrm{Co(hen)(NCS)_2}$	Dark green	25·8	4·3	20·1	27·7	4·7	20·35		
* $\mathrm{Zn(hen)_2Br_2}$	White	22·25	5·55	12·95	22·35	5·3	13·2		
* Zn(hen-H)Br	White	19·3	4·45	11·3	19·55	4·75	11·45		
* Ni(hen + acetone − $\mathrm{H_2O)_2Br_2}$	Pink	31·95	6·5	10·7	31·9	6·3	11·3	3·15	264
* Cu(hen + acetone − $\mathrm{H_2O)_2Br_2H_2O}$ [e]	Blue-mauve	31·7	6·43	10·6	31·6	6·4	10·0	1·92	288
Cu(hen + acetone − $\mathrm{H_2O)_2Cl_2H_2O}$ [f]	Blue-mauve	38·1	7·76	12·7	37·9	7·9	12·8	1·84	
* Zn(hen + acetone − $\mathrm{H_2O)Cl_2}$ [g]	White	27·0	5·71	10·0	26·6	5·55	10·1		

* New compounds.

[a] Cl: Found 27·9, Expected 28·2%. [b] Cu: Found 18·3, Expected 18·5%. [c] Cu: Found 37·05, Expected 37·05, halide: Found 14·65, Expected 14·75%. [d] Cu: Found 21·7, Expected 21·8%. [e] Cu: Found 11·7, Expected 12·0%. [f] Cu: Found 14·4, Expected 14·5%. [g] Zn: Found 23·4, Expected 23·3%.

Typical conductance values for 2 : 1 electrolytes in aqueous solution lie in the range 240—280.

TABLE 2

Electronic and infrared spectra

Complex	$d \longrightarrow d$ bands kK	ν_{OH} (free ligand)	$\nu_{OH}(H_2O)$	ν_{N-H}	$\nu_{C=N}$	δ_{NH_2}
$\mathrm{Ni(hen)_3Cl_2}$	10·9s, 17·9s, 28·4s	3380s		3290m		1594s
$\mathrm{Ni(hen)_3Br_2}$	10·9s, 17·8s, 28·5s	3380s		3340w		1590s
$\mathrm{Ni(hen)_2Br_2(A)}$	8·3sh, 11·0s, 17·2s, 27·5s			3210, 3190		1577m
$\mathrm{Ni(hen)_2Br_2(B)}$	8·6sh, 11·0s, 17·7s, 22·4sh					
$\mathrm{Ni(hen)_2(NO_3)_2}$	8·4sh, 11·1s, 17·7s, 28·2s			3290m		1595m
$\mathrm{Ni(hen)_2(ClO_4)_2(A)}$	8·5sh, 11·2s, 17·5s, 27·7s			3330m		1585m
$\mathrm{Ni(hen)_2(ClO_4)_2(B)}$	10·7s, 17·4s, 22·9sh			3300m		
$\mathrm{Ni(hen)Cl_2,H_2O}$	8·2sh, 10·5s, 15·4s, 25·3s		3350w,br	3300		1582m
$\mathrm{Ni(hen)Br_2H_2O}$	8·2sh, 10·7s, 15·6s, 25·3s		3330w,br	3275		1582m
$\mathrm{Ni(hen)Cl_2}$	9·5s, 15·2s, 24·9s			3240s		1590m
$\mathrm{Ni(hen)Br_2}$	7·4w, 10·3s, 14·9s, 24·0s			3220s		1585m
$\mathrm{Cu(hen)_2Cl_2}$	17·7s, 23·0sh			3300m		1595m
$\mathrm{Cu(hen)_2Br_2}$	18·4s, 22·6sh			3275m		1580m
$\mathrm{Cu(hen)_2(NO_3)_2}$	16·2s, 23·0sh			3240s		1598m
$\mathrm{Cu(hen)_2(ClO_4)_2}$	15·8s, 23·0sh	3540s? 3370s		3310s		1595m
$\mathrm{Cu(hen)_2(NO_3)_2H_2O}$	16·4s, 22·7sh		3310m 3290sh	3240m		1605br
$\mathrm{Cu(hen)(NO_3)_2}$	15·2s, 23·0sh			3240m		1600br
$\mathrm{Cu(hen)Cl_2}$	14·7s, 23·1w	3400s		3190m		1590m
$\mathrm{Co(hen)Cl_2}$	5·2sh, 6·3s, 7·4sh, 14·3s, 15·5sh			3320s		1590m
$\mathrm{Co(hen)Br_2}$	4·8sh, 5·8s, 7·5sh, 14·2s, 15·4sh, 17·2sh			3200m		1587m
$\mathrm{Co(hen)(NCS)_2}$	6·9sh, 7·6s, 8·8sh, 16·0s, 16·4sh, 17·1sh			3200br		1582m
$\mathrm{Zn(hen)_2Br_2}$				3260m		1550w
$\mathrm{Zn(hen\text{-}H^+)Br}$				3260m		1580w
Ni(hen + acetone − $\mathrm{H_2O)_2Br_2}$	9·5s, 19·0s, 22·6sh			3200m	1655	
Cu(hen + acetone − $\mathrm{H_2O)Cl_2H_2O}$			3400s,br		1660	
Cu(hen + acetone − $\mathrm{H_2O)Br_2,H_2O}$	18·2s		3270w	3160m	1660	
Zn(hen + acetone − $\mathrm{H_2O)Cl_2}$		3460s		3220m 3210m	1650	

water molecule is replaced by one halide, giving [Ni(hen)X]X.

The copper 1 : 1 complexes involve co-ordinated anions as indicated in the appropriate cases by the i.r. spectrum of the nitrate group and the presence of a band at 341 cm^{-1}, in the far-i.r. spectrum, assignable to ν_{CuCl}. The nitrato-complex shows no band in the i.r. region assignable to free ν_{OH}. Presumably it is a six-co-ordinate complex with one bidentate and one unidentate nitrato-group. The chloro-complex contains bidentate ligand, as is demonstrated by the band at 3400 cm^{-1}, rather than terdentate ligand as suggested by Breckenridge. The position of the metal–chlorine stretching frequency rules out the possibility of bridging halides, so it appears that this has a square planar structure.

The cobalt complexes are aquo complexes $[Co(hen)H_2O]X_2$, the water being replaced readily by the halide or pseudohalide ion on heating, with appropriate weight loss. The species $Co(hen)X_2$ are of tetrahedral stereochemistry, while the anion dependence of the *d–d* bands shows the anions to be co-ordinated. Their magnetic moments are very close to the spin only value. This may indicate [7] that the complexes are extremely distorted. The analytical data for carbon is poor. The zinc complex is the only one having deprotonated ligand, the oxygen proton being lost. The complex is assumed to be of tetrahedral stereochemistry.

Condensation of Acetone with Co-ordinated N-*hydroxyethylethylenediamine*.—We have prepared the following complexes in which condensation has occurred between ligand and acetone: NiL_2Br_2,CuL_2X_2,H_2O (X = Cl, Br) and $ZnLCl_2$, where L = (hen + acetone − H_2O). Patel and Curtis have prepared CuL_2X_2,H_2O (X = NO_3,ClO_4) and have formulated them as (I) in which the co-ordinated amine groups are bridged *via* a diacetone amine-imine group as observed for a range of co-ordinated amines and carbonyl compounds.[8] In each of the present examples the i.r. spectrum confirms that condensation has occurred, showing a new band that may be assigned to $\nu_{C=N}$ and the disappearance of bands associated with the primary amine group. We cannot confirm the amine-imine bridge by observation of the secondary amine bands as an NH group is already present in the molecule. The i.r. spectrum of the nickel complex also shows that the OH group is co-ordinated. The spectra of the copper complexes are complicated by the presence of the water molecule but also indicate the presence of co-ordinated OH. The electronic spectra and magnetic moments of all three complexes are consistent with an octahedral stereochemistry, and so it appears that they involve the linear hexadentate ligand 7,9,9-trimethyl-3,6,10,13-tetra-azapentadeca-6-en-1,15-diol.

The zinc complex, of 1 : 1 stoicheiometry, cannot involve this ligand. Condensation of acetone with the NH_2 group has occurred, presumably forming the Schiff base. The OH group of the ligand is not co-ordinated (ν_{OH} at 3460 cm^{-1}) while we assign bands in the i.r. spectrum at *ca.* 300 cm^{-1} to ν_{ZnCl}. The complex thus appears to be of tetrahedral stereochemistry.

We have investigated the stability of these complexes in aqueous solution. The 1 : 1 complex with $ZnCl_2$ is hydrolysed readily giving acetone, but the complex with $CuCl_2$ is stable at 50 °C. This provides additional evidence [8] for the existence of the amine-imine bridge in the latter case.

Condensation of Acetone with N-*Hydroxyethylethylenediamine*.—This condensation occurs readily in the absence of metal ion, giving a monomeric species of molecular weight 152 (in chloroform, in the concentration range 0·25—1% by weight). We were unable to prepare complexes with this ligand, only obtaining complexes of *N*-hydroxyethylethylenediamine. This may be understood in terms of the co-ordination to the metal facilitating hydrolysis, with the generation of acetone and co-ordinated *N*-hydroxyethylethylenediamine, before the system is stabilised by the formation of the amine-imine bridge.

The formation of complexes of 7,9,9-trimethyl-3,6,10,13-tetra-azapentadeca-6-en-1,15-diol must be accounted for by a different scheme in view of the above results. One path involves a prior self-condensation of acetone to give diacetone alcohol which then condenses with the co-ordinated *N*-hydroxyethylethylenediamine in a metal-ion organised reaction. This is consistent with the observation that metal–hen complexes were formed prior to the production of complexes of the hexadentate ligand in the preparations involving refluxing metal salt and hen in acetone. We have also shown that refluxing complexes of hen in diacetone alcohol results in the rapid formation of complexes of 7,9,9-trimethyl-3,6,10,13-tetra-azapentadeca-6-en-1,15-diol, but such a result is open to a number of interpretations in view of the instability of diacetone alcohol.

The formation of Zn(hen + acetone − H_2O)Cl_2 by refluxing the zinc hydroxyethylethylenediamine complex in acetone is unexpected in the light of the preceding comments. It is significant that this complex is of tetrahedral stereochemistry. The tetrahedral bond angle will satisfy the requirements of the condensed ligand more easily than will the octahedral bond angle, in view of the planar trigonal arrangement required around the nitrogen atom of the N=C group in the ligand. This may well contribute to the instability of octahedral complexes of $HO{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}N{=}CMe_2$.

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[7] B. N. Figgis, 'Introduction to Ligand Fields,' Interscience, New York, 1966, 275.

[8] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.