Some Metal-ion Complexes with Ligands formed by Reaction of Amines with Aliphatic Carbonyl Compounds. Part V.[1] Nickel(II) β-Hydroxyimine Complexes formed by Reaction of Amine Complexes with 4-Hydroxy-4-methylpentan-2-one

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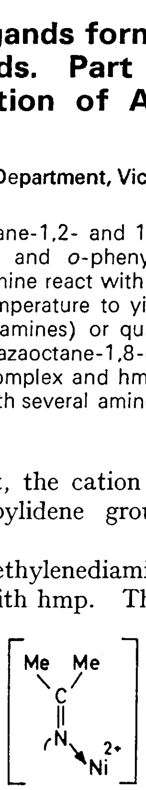
Bis complexes of nickel(II) with ethylenediamine, propane-1,2- and 1,3-diamine, *iso*, *meso*, and probably *rac*-dimethylethylenediamine, 1,2-diphenylethylenediamine, and *o*-phenylenediamine, and mono complexes of 4-azaheptane-1,7-diamine and 3,6-diazaoctane-1,8-diamine react with 4-hydroxy-4-methylpentan-2-one (hmp) (diacetone alcohol) over a period of hours at room temperature to yield complexes of β-hydroxyimines. The hydroxy-groups are co-ordinated to give tridentate (diamines) or quinquedentate ligands (4-azaheptane-1,7-diamine with two β-hydroxyimino-groups, and 3,6-diazaoctane-1,8-diamine with one). The complexes are hydrolysed, more or less rapidly, to reform the amine complex and hmp. Nickel(II) complexes of several other triamines and tetra-amines, and copper(II) complexes with several amines, do not react with hmp under the same conditions.

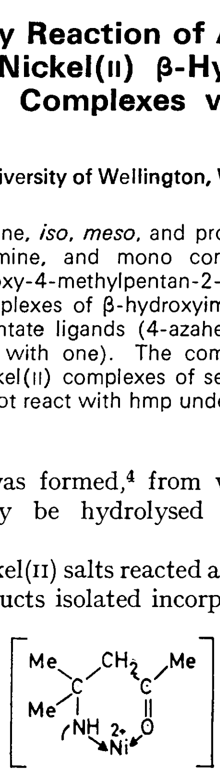
COMPLEXES formed by reaction of nickel(II) derivatives of a number of amines with acetone have been described.[2] These are of three main types: with *N*-isopropylideneamino-groups, (I);[3] with β-aminoketones, (II),[4-6] and those linked by a β-amino–imino-bridge, (III).[2-6] It was suggested that the reactions follow the sequence (I) ⟶ (II) ⟶ (III), an initially formed imine undergoing an aldol-type reaction to form the β-aminoketone, which then undergoes an intramolecular imine-formation reaction.[4] Complexes of type (II) amd (III) contain the acetone residues as a dimeric unit, and therefore comparative reactions of the acetone dimers 4-hydroxy-4-methylpentan-2-one (hmp) (diacetone alcohol) and 4-methylpent-3-en-2-one (mpo) (mesityl oxide) are of some interest. Previously reported reactions of nickel amine complexes with hmp have yielded derivatives of type (III).[7] We here report reactions of a number of nickel(II) amine complexes with hmp under very mild conditions to yield complexes of β-hydroxyimines, (IV). Related complexes formed from some α-hydroxyketones have previously been described.[8]

RESULTS AND DISCUSSION

Reactions with Ethylenediamine Complexes.—Tris(ethylenediamine)nickel(II) salts reacted with acetone over a period of days at room temperature to yield the macrocyclic cation (V) and its 4,14-diene isomer,[9] with the cation (VI) occurring in the reaction mixture at earlier stages.[4] Busch reported that tris(ethylenediamine)nickel(II) salts react with hmp when heated under reflux in methanol to yield salts of the macrocyclic cation (V), or the linear quadridentate (VII). With mpo as reactant, considerable ' deterioration ' of mpo occurred and only (VII) was isolated.[7] Bis(ethylenediamine)nickel(II) salts reacted with acetone in a period of hours at room temperature. In the absence of co-ordinating anions or solvents, the bis(β-aminoketone) cation (VIII) was formed. At higher temperatures, or in the presence of co-ordinating anions or solvent, the cation (VI) was formed,[4] from which the isopropylidene group may be hydrolysed to yield (VII).

Bis(ethylenediamine)nickel(II) salts reacted at a similar rate with hmp. The products isolated incorporate two hmp residues with the perchlorate or nitrate as starting material, (IX), one hmp residue starting with the chloride, bromide, or thiocyanate, (X). The i.r. spectra of the diperchlorate salt of (IX) showed bands assigned to $\nu(NH_2)$ and $\delta(NH_2)$ of co-ordinated primary amino-groups, a strong band near 1 660 cm^{-1} assigned to $\nu(C{=}N)$ of a co-ordinated imino-group, and a strong band at 3 430 cm^{-1} assigned to $\nu(OH)$. The diperchlorate salt of (VIII) was distinctly different from, although isomeric with, the hmp condensation product (IX) in crystal form, spectroscopic properties, *etc.* Furthermore, the salt of (VIII) underwent a cyclization reaction in co-ordinating solvents such as pyridine to form the macrocyclic cation (V),[4] while (IX) was simply hydrolysed to form, for example, bis(ethylenediamine)dipyridinenickel(II) perchlorate and hmp.


(I)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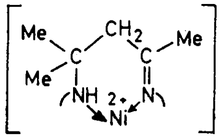
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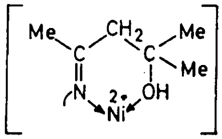
(IV)

The properties of complex (IX) therefore suggest that the hmp condensation products contain β-hydroxyimino-groups. The complexes are blue-violet, with

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[1] Part IV, N. F. Curtis, *J.C.S. Dalton*, 1974, 347.

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

[3] D. A. Howe and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 223.

[4] N. F. Curtis, *J.C.S. Dalton*, 1972, 1357.

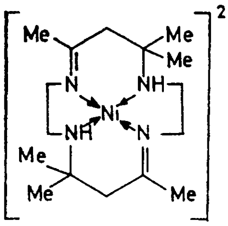
[5] N. F. Curtis, *J.C.S. Dalton*, 1973, 863.

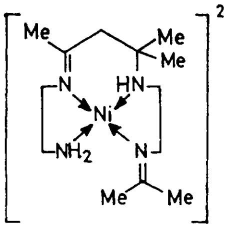
[6] D. F. Cook and N. F. Curtis, *J.C.S. Dalton*, 1973, 1076.

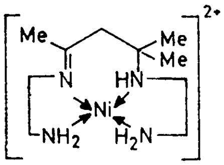
[7] T. E. MacDermott and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 1115.

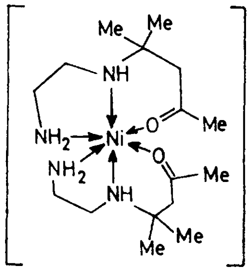
[8] T. E. MacDermott, B. E. Sewall, and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 5784.

[9] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc.* (*A*), 1966, 1015.


(V)

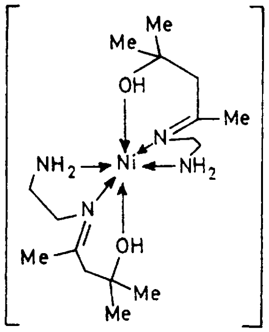

(VI)

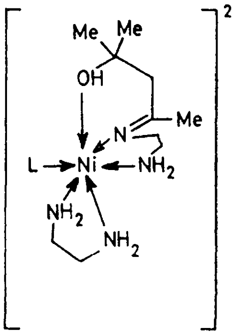

(VII)


(VIII)

d-d spectra (Table) and magnetic susceptibilities (see Experimental section) typical of pseudo-octahedral triplet-ground-state nickel(II) derivatives. It is therefore concluded that the fifth and sixth co-ordination sites are occupied by the hydroxy-groups of the ligand in cation (IX), or by the hydroxy-group of the ligand and an anion or water molecule in (X). The i.r. spectrum of the nitrate salts of (IX) showed bands typical of ionic nitrate, and it is assigned a structure analogous to the perchlorate with a water molecule of crystallization.

The tridentate ligand $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C(Me){\cdot}CH_2{\cdot}C(OH)Me_2$ in complexes (IX) and (X) could be present in the *meridional* or *facial* arrangements. For cation (IX), the meridional arrangement can occur in only one configuration (ignoring the chiral secondary amino-groups), which places both the hydroxy- and primary amino-groups *cis*. The *facial* arrangement could occur in three configurations: (*a*) with both the hydroxy- and primary amino-groups *cis*; (*b*), with the hydroxy-groups *cis* and the primary amino-groups *trans*; and (*c*) with the hydroxy-groups *trans* and the primary amino-groups *cis*. The reflectance spectra of the diperchlorate and dinitrate hydrate salts of (IX) both showed the ν_1 band ($^3T_{2g}{\leftarrow}^3A_{2g}$ of O_h) present as a doublet. For the NiN_4O_2 chromophore this indicates that the oxygen-donor atoms are in *trans* sites, supporting assignment of the *facial* configuration (*c*), as represented. In contrast, the reflectance spectrum of the diperchlorate salt of (VIII) had ν_1 as a singlet, indicating that this cation adopts a configuration with the oxygen-donor atoms *cis*.[4] Complexes (X), isolated with chloride, bromide, or thiocyanate as anion, showed no splitting of the ν_1 band of the reflectance spectrum. The chloride and bromide are therefore assigned structures (X) with an anion or water molecule *cis* to the hydroxy-group, assuming that the β-hydroxyimine retains the *facial* co-ordination present in (IX). The structure of the thiocyanate is discussed below.


(IX)


(X) L = H_2O or anion

Analytical data (%) [a] and reflectance spectra (band maxima/10^3 cm^{-1})

Compound	C	H	Ni	ν_1 [b,c]	ν_2 [b,d]	ν_3 [b,e]
(IX) $[ClO_4]_2$	33·4 (33·5)	6·4 (6·3)	10·3 (10·2)	9·0, 10·8	17·4	*ca.* 29 [f]
(IX) $[NO_3]_2{\cdot}H_2O$	37·2 (37·2)	7·4 (7·4)	11·6 (11·4)	9·3, 10·8	17·8	*ca.* 28
(X) $Cl_2{\cdot}H_2O$	33·5 (33·5)	7·3 (7·6)	16·0 (16·0)	11·0	17·7	
(X) $Br_2{\cdot}H_2O$	26·1 (26·4)	6·1 (6·2)	13·1 (12·9)	10·8	17·6	
(X) $[NCS]_2$	36·6 (36·6)	6·6 (6·7)	14·9 (15·0)	11·9	17·8	
(XI) $[ClO_4]_2{\cdot}H_2O$	34·6 (34·9)	6·5 (6·8)	9·6 (9·5)	9·3, 11·2	17·4	28·2
(XII) $[NCS]_2{\cdot}H_2O$	38·7 (38·4)	7·4 (7·4)	13·5 (13·4)	11·0	17·6	
(XIII) $[ClO_4]_2$	37·7 (38·1)	7·0 (7·1)	9·4 (9·3)	10·7	17·2	27·2
(XIV) $[ClO_4]_2$	38·1 (38·1)	6·9 (7·1)	9·5 (9·3)	9·3, 10·8	17·2	27·4
(XV) $[ClO_4]_2$	42·8 (43·0)	5·8 (5·4)	8·8 (8·8)	11·4	17·0	
(XVI) $[ClO_4]_2{\cdot}2H_2O$	52·4 (52·5)	6·4 (6·2)	6·3 (6·4)	10·6	16·9	27·2
(XVII) $[ClO_4]_2{\cdot}2H_2O$	35·8 (35·9)	6·5 (6·7)	10·0 (9·8)	10·0	16·7	26·6
(XVIII) $[ClO_4]_2{\cdot}H_2O$	35·7 (35·8)	6·6 (6·5)	9·8 (9·7)	8·7	15·9	25·7
(XIX) $[ZnCl_4]{\cdot}H_2O$	27·3 (27·3)	5·9 (5·7)	10·9 (11·1)	10·7	17·0	

[a] Calculated values are given in parentheses. [b] Assignments in O_h. [c] $^3T_{2g}{\leftarrow}^3A_{2g}$. [d] $^3T_{1g}{\leftarrow}^3A_{2g}$. [e] $^3T_{2g}(P){\leftarrow}^3A_{2g}$. This band was often obscured by charge-transfer absorption. [f] *Cf.* 10·5, 17·4, and 29·4 10^3 cm^{-1} for the diperchlorate salt of (VIII).[4]

The cation (IX) was hydrolysed only slowly in water, and the diperchlorate could, for example, be recrystallized from hot water, albeit in low yield. This resistance to hydrolysis is unusual for imino-complexes, and must be attributed to a stabilizing effect arising from co-ordination of the hydroxy-group. The imino-groups of (IX) were reduced by sodium tetrahydroborate in methanol with formation of a bis(β-hydroxyamine) complex. Busch reported that when an ethylene glycol solution of the related α-hydroxyimine complex was boiled to dryness, an amino-imino-complex related to (III) was formed.[8] Attempts to cause similar pyrolysis reactions with complexes (IX) or (X) were unsuccessful. Attempts to react a variety of mono(ethylenediamine)-nickel(II) complexes with hmp were also unsuccessful.

Reactions with Propane-1,2-*diamine Complexes*.—Bis(propane-1,2-diamine)nickel(II) complexes reacted similarly to their ethylenediamine (en) analogues with hmp, as with acetone.[5] A bis(β-hydroxyimino) complex, (XI), was isolated with perchlorate, and a mono(β-hydroxyimino) complex, (XII), with thiocyanate. The i.r. and *d–d* electronic spectra and chemical properties of the diperchlorate hydrate salt of (XI) were similar to those of the en analogue (except that it is hydrated).

The mono(β-hydroxyimino) thiocyanate salts formed with en and propane-1,2-diamine (pn) appear to be structurally different. The en derivative showed doublet ν(C≡N) and ν(CS) bands in the i.r. spectrum (2 101vs, and 2 069vs; 767w and 750w cm^{-1}) and bands in the reflectance spectrum were shifted to higher energy compared with the chloride or bromide. These facts suggest that the complex has a structure with one thiocyanate *N*-co-ordinated, and the other ionic. Alternatively, both the thiocyanate ions could be co-ordinated in the *cis*-configuration, with the hydroxy-group not co-ordinated. This possibility is considered to be less likely because the stabilizing effect arising from the chelation of the hydroxy-group would be absent. The pn derivative contains a molecule of water; the reflectance spectrum was very similar to those of the en chloride and bromide derivatives, and the i.r. spectrum showed singlet ν(C≡N) and ν(CS) bands (2 095vs; 777 cm^{-1}). These results suggest that in this case the water molecule is co-ordinated, with the thiocyanate all ionic. Alternatively, both the thiocyanate ions could be co-ordinated in the *trans*-configuration with the hydroxy-group not co-ordinated. As for the en compound, this is considered to be less likely. The ν(CS) wavenumbers was somewhat high for ionic thiocyanate, but these wavenumbers are sensitive to hydrogen bonding and lattice interactions.

The pn (β-hydroxyimine) ligand could have the methyl group of the pn residue α or β with respect to the imino-group, the β-arrangement which minimizes intraligand interactions being presumed. [For macrocyclic complexes analogous to (V), derived from pn, this methyl group is α to the imino-group,[10] but this arrangement is presumed to arise because the initial imine is formed with this group β. The reaction sequence (I) ⟶ (II) ⟶ (III) converts this imino-group to a secondary amino-group, and the imino-groups of the macrocycle arise from the second amino-group, α to this methyl group.] [5]

Reactions with 1,1-*Dimethylethylenediamine Complexes*.—The bis(1,1-dimethylenediamine)nickel(II) cation showed no reaction with acetone over a prolonged period at room temperature. At higher temperatures, or with the tris complex, reaction occurred to form a linear quadridentate related to (VII).[11] Bis(1,1-dimethylenediamine)nickel(II) perchlorate reacted with hmp over a period of hours at room temperature to form a bis(β-hydroxyimino) cation, (XIII). This is much more readily hydrolysed than the en analogue and, for example, is slowly hydrolysed if exposed to the atmosphere. This complex showed the ν_1 band of the reflectance spectrum as a singlet and is therefore assigned a structure with the hydroxy-groups *cis*, the difference from the en and pn derivatives presumably arising from a steric interaction involving the axial-methyl substituents on the five-membered chelate rings (presumed to be remote from the imino-group).

Reactions with sym-1,2-*Dimethylethylenediamine Complexes*.—All attempts to isolate products of reactions between acetone and bis or tris complexes of *meso*- or *rac–sym*-1,2-dimethylethylenediamine with nickel(II) have been unsuccessful.[2] However, the bis complexes as perchlorates reacted rapidly with hmp. For the *meso*-compound, a readily hydrolysed bis(β-hydroxyimino) complex, (XIV), was isolated, but for the *rac*-isomer the product was very readily hydrolysed and was not isolated pure. The reflectance spectrum of diperchlorate salt of (XIV) showed the doublet ν_1 band, indicative of a structure analogous to (IX). For the *meso*-amine, both methyl groups of the diamine residue can occur as equatorial substituents of the *gauche*-conformation five-membered chelate ring, which presumably accounts for the greater stability of this configuration compared with that derived from the *rac*-amine where one of these groups must be axial.

Reactions with o-*Phenylenediamine and* meso-1,2-*Diphenylethylenediamine Complexes*.—Again no products of reaction of nickel(II) complexes of these amines with acetone have been isolated. The bis(diamine)nickel(II) perchlorate salts reacted rapidly with hmp to form readily hydrolysed bis(β-hydroxyimino) complexes (XV) from *o*-phenylenediamine and (XVI) from 1,2-diphenylethylenediamine. The reflectance spectra of the diperchlorates showed singlet ν_1 bands, indicative of *cis*-siting of the hydroxy-groups.

Reactions with Propane-1,3-*diamine Complexes*.—Bis(propane-1,3-diamine)nickel(II) complexes react rapidly with acetone to form complexes of type (I). For the tris complexes, further reaction occurs slowly, ultimately forming a macrocyclic cation.[6] Bis(propane-1,3-diamine)nickel(II) perchlorate reacted rapidly with hmp at room temperature to form a bis(β-hydroxyimino) complex, (XVII). The product is more readily hydrolysed than the en or pn derivatives, but less readily than the dimethylethylenediamine derivatives. The reflectance spectrum of the diperchlorate showed a singlet ν_1 band, indicating *cis*-arrangement of the hydroxy-groups. Similar reactions appeared to occur for salts with other anions, but the products were very soluble and were not isolated.

Reactions with 4-*Azaheptane*-1,7-*diamine Complexes*.—Bis(4-azaheptane-1,7-diamine)nickel(II) perchlorate reacts with acetone to form a product formulated as bis(*N*-isopropylideneamino) complex, apparently present as

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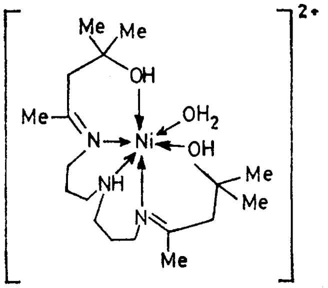
[10] D. A. Swann, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 2133.

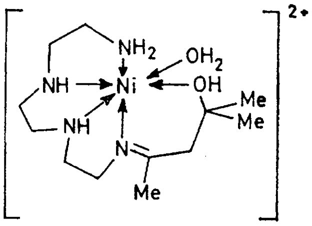
[11] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 1204.

a hydroxy-bridged dimer.[12a] Work supporting assignment of a different (macrocyle) structure for this complex will be published shortly.[12b] Mono(4-azaheptane-1,7-diamine)nickel(II) perchlorate reacted with hmp to form a bis(β-hydroxyimino) complex, (XVIII), which crystallized with one molecule of water. The reflectance spectrum for the diperchlorate was as expected for the NiN_3O_3 chromophore, and therefore the complex is assigned the structure shown with the water molecule occupying the sixth co-ordination site (a number of alternate configurations are possible). The compound has resistance to hydrolysis comparable with that of the propane-1,3-diamine derivative, (XVII).



[(XVIII)(H_2O)]

Reactions with 3,6-*Diazaoctane*-1,8-*diamine* (*Triethylenetetramine, trien*) *Complexes*.—Orange mono(3,6-diazaoctane-1,8-diamine)nickel(II) perchlorate [13] dissolved in hmp to form a blue-violet solution. This *could* contain species with (β-hydroxyimino)-groups, or could have discrete hmp molecules filling the two additional co-ordination sites, as occurs for methanol or ethanol.[13] Addition of excess of propan-2-ol caused the colour to change to orange and unchanged starting material to crystallize, favouring the second possibility. In contrast, orange [Ni(trien)][$ZnCl_4$] [14] reacted slowly (it is sparingly soluble) with hmp to form a violet product, (XIX), which had properties expected of a mono(β-hydroxyimino) derivative. The same complex was formed by reaction of [Ni(trien)]Cl_2 with hmp, the product being isolated on addition of zinc(II) chloride. The complex is hydrated, the water molecule presumably occupying the sixth co-ordination site. The reflectance spectrum of the tetrachlorozincate(II) salt showed a singlet ν_1 band, indicating that the two oxygen-donor atoms are *cis* (several configurations are possible). The complex shows resistance to hydrolysis comparable with that of the en derivative, (IX).



[(XIX)(H_2O)]

I.r. Spectra.—The i.r. spectra of all the complexes show a strong broad band assigned to ν(OH) near 3 340 cm^{-1}. This often overlay bands assigned to ν(OH) of water, where present, and ν(NH). Spectra also showed a strong band at 1650 ± 10 cm^{-1}, assigned to ν(C=N) of the imino-group, and a band near 1590 cm^{-1} assigned to $\delta(NH_2)$ [except for the (XIX) salt which has no primary amino-group].

Attempted Reaction with Other Amines.—Attempts to isolate β-hydroxyimino-complexes from mono complexes of nickel(II) with 3-azapentane-1,5-diamine (diethylenetriamine), 3-azahexane-1,6-diamine, 3,6-diazanonane-1,9-diamine, 3,7-diazanonane-1,9-diamine (XX), 4,7-diazadecane-1,10-diamine (XXI), and 4,8-diazaundecane-1,11-diamine (XXII) were not successful. For comparison the complex $[Ni_2(XX)_3]^{2+}$ reacted with acetone, hmp, or mpo to form a macrocyclic complex,[15] and complexes of (XXI) and (XXII) reacted with acetone to form *N*-isopropylideneamino complexes; complexes of the other amines showed no reaction.

Attempted Reactions of Copper(II) *Complexes*.—Attempts to prepare β-hydroxyimino-complexes by reaction of mono- and bis-(ethylenediamine), bis(propane-1,3-diamine), and 3,6-diazaoctane-1,8-diamine complexes of copper(II) with hmp were unsuccessful. In many cases complexes of these amines react with acetone to form *N*-isopropylideneamino, β-aminoketone, or β-amino–imino-derivatives.[2-7,12-16]

Conclusions.—Nickel(II) complexes of a variety of di-, tri-, and tetra-amines react with hmp under very mild conditions to form β-hydroxyimino-complexes. These are formed only where less than six amino-donor groups are present, and the resulting β-hydroxyimines are stabilized by co-ordination of the hydroxy-group, forming an additional six-membered chelate ring. Reaction occurred for all diamines tested, although derivatives of the more sterically hindered amines are more readily hydrolysed. Complexes of 4-azaheptane-1,7-diamine and 3,6-diazaoctane-1,8-diamine react similarly, although other tri- and tetra-amines tested show no reactivity.

Differing, but isomeric, products are formed when bis(ethylenediamine)nickel(II) perchlorate reacts with acetone and with hmp. This confirms that the β-aminoketone product obtained with acetone is formed by reaction with acetone molecules, and not with preformed hmp (metal amine complexes are known to catalyse formation of hmp from acetone). The reactivities of the nickel(II) amine complexes with acetone and with hmp are quite variable. Thus, with some amines, reaction occurs for both carbonyl compounds, for others

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[12] (*a*) N. F. Curtis and D. A. House, *J. Chem. Soc.*, 1965, 5502; (*b*) J. H. Johnston, J. W. L. Martin, and N. F. Curtis, to be published.

[13] N. F. Curtis and D. A. House, *J. Chem. Soc.*, 1965, 6194.

[14] D. A. House and N. F. Curtis, *J. Chem. Soc.*, **1963**, **4109**.

[15] N. F. Curtis and N. B. Milestone, to be published.

[16] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1962, **84**, 3248.

reaction occurs for one and not for the other, while for some, such as 3-azapentane-1,5-diamine, reaction occurs with neither. In some cases the differences can to some extent be explained by the separation of sparingly soluble products, but in others the explanation of the difference is not obvious.

EXPERIMENTAL

Analytical data are listed in the Table.

The complexes *bis*(7-*amino*-2,4-*dimethyl*-5-*azahept*-4-*en*-2-*ol*)*nickel*(II) *diperchlorate* and *dinitrate hydrate*, (IX) $[ClO_4]_2$ and (IX) $[NO_3]_2 \cdot H_2O$, *bis*(7-*amino*-2,4-*dimethyl*-5-*azaoct*-4-*en*-2-*ol*)*nickel*(II) *diperchlorate hydrate*, (XI) $[ClO_4]_2 \cdot H_2O$, *bis*(7-*amino*-2,4,7-*trimethyl*-5-*azaoct*-4-*en*-2-*ol*)-*nickel*(II) *diperchlorate*, (XIII) $[ClO_4]_2$, *bis*(rac-7-*amino*-2,4,6-*trimethyl*-5-*azaoct*-4-*en*-2-*ol*)*nickel*(II) *diperchlorate*, (XIV) $[ClO_4]_2$, *bis*[N-(3-*hydroxy*-1,3-*dimethylbutyl*)-o-*phenylenediamine*]*nickel*(II) *diperchlorate*, (XV) $[ClO_4]_2$, *bis*(meso-7-*amino*-2,4-*dimethyl*-6,7-*diphenyl*-5-*azahept*-4-*en*-2-*ol*)*nickel*(II) *diperchlorate dihydrate*, (XVI) $[ClO_4]_2 \cdot 2H_2O$, *bis*(8-*amino*-2,4-*dimethyl*-5-*azaoct*-4-*en*-2-*ol*)*nickel*(II) *diperchlorate*, (XVII) $[ClO_4]_2$, (7-*amino*-2,4-*dimethyl*-5-*azahept*-4-*en*-2-*ol*)*aqua*(*ethylenediamine*)*nickel*(II) *dichloride* and *dibromide* $[(X)(H_2O)]Cl_2$ and $[(X)(H_2O)]Br_2$, (7-*amino*-2,4-*dimethyl*-5-*azahept*-4-*en*-2-*ol*)(*ethylenediamine*)*isothiocyanatonickel*(II) *thiocyanate*, [(X)NCS][SCN], and (7-*amino*-2,4-*dimethyl*-5-*azaoct*-4-*en*-2-*ol*)*aquanickel*(II) *thiocyanate*, $[(XII)(H_2O)][SCN]_2$, were preprepared as follows. The appropriate bis(diamine)nickel(II) salt was treated at room temperature with 4-hydroxy-4-methylpentan-2-one (hmp) or hmp–methanol (1 : 1). The products crystallized out over 1—2 d, or were precipitated on addition of propan-2-ol after *ca.* 2 d, in high yield. With *o*-phenylenediamine the solution darkened because of polymer formation. In the other cases the products could be left in the reaction mixture for prolonged periods without further change. The *products* were recrystallized from hot methanol–propan-2-ol.

Aqua(2,4,14,16-*tetramethyl*-5,9,13-*triazaheptadeca*-4,13-*diene*-2,16-*diol*)*nickel*(II) *Diperchlorate*, $[(XVIII)(H_2O)][ClO_4]_2$.—This complex was prepared similarly, from mono-(4-azaheptane-1,7-diamine)nickel(II) perchlorate, prepared *in situ* by reaction of equimolar amounts of the bis complex and nickel(II) perchlorate. The reaction took *ca.* 5 d at room temperature, and the *product* was recrystallized from hot ethanol.

(13-*Amino*-2,4-*dimethyl*-5,8,11-*triazatridec*-4-*en*-2-*ol*)*aquanickel*(II) *Tetrachlorozincate*(II), $[(XIX)(H_2O)][ZnCl_4]$.—This complex was prepared by treating mono(3,6-diazaoctane-1,8-diamine)nickel(II) tetrachlorozincate(II) [Ni(trien)]-$[ZnCl_4]$ [13] with hmp–methanol at room temperature. The starting material dissolved and the product crystallized over 1—2 weeks. The *product* was recrystallized from hot ethanol.

Magnetic Susceptibilities.—The magnetic susceptibilities of three representative complexes were measured at 23·5 °C. The magnetic moments were normal for triplet ground state, pseudo-octahedral, nickel(II) complexes: (IX) $[ClO_4]_2$, $\chi_g = 5{\cdot}972 \times 10^{-6}$, $\mu_{eff.} = 2{\cdot}86$; (XII) $[NCS]_2$, $\chi_g = 8{\cdot}185 \times 10^{6}$, $\mu_{eff.} = 2{\cdot}93$; and (XVII) $[ClO_4]_2$, $\chi_g = 6{\cdot}208 \times 10^{-6}$ c.g.s.u., $\mu_{eff.} = 2{\cdot}99$ B.M.; calculated from the Curie law with correction for diamagnetism.*

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* 1 B.M. = $0{\cdot}927 \times 10^{-23}$ A m^2.