Some Metal-ion Complexes with Ligands formed by Reaction of Amines with Aliphatic Carbonyl Compounds. Part II.[1] Some Nickel(II) and Copper(II) Compounds formed by the 1,2-Diaminopropane–Acetone Reaction

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Reaction of bis(1,2-diaminopropane)nickel(II) with acetone yields the bis-complex of the β-amino-ketone $NH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}NH{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ which acts as a tridentate ligand. In pyridine this is converted into the nickel(II) complex of the macrocyclic ligand *C-meso*-3,5,7,7,10,12,14,14-octamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene, L. The bis(*R*-1,2-diaminopropane) complex reacts to form an analogous β-amino-ketone complex which in pyridine yields the *RR*-enantiomorph of the nickel(II) complex of *C-rac*-L. The tris(1,2-diaminopropane)nickel(II) and copper(II) complexes react with acetone to yield a mixture of two products. These are *C-meso*- and *C-rac*-$[M(L)]^{2+}$ for nickel(II), and probably also for copper(II).

In Part I,[1] reactions of nickel(II) and copper(II) diaminoethane complexes with acetone were described, and previous work [2] on the topic summarised. Similar reactions with acetone of 1,2-diaminopropane † complexes of nickel(II) and copper(II) are reported here.

Bis-(1,2-diaminopropane)nickel(II)–Acetone Reaction.—A reaction of bis-(1,2-diaminopropane)nickel(II) perchlorate ‡ with acetone at 110° to yield initially the cation $[Ni(\mathbf{1})]^{2+}$ and finally the cation $[Ni(\mathbf{2})]^{2+}$ has been reported.[3] The salts $[Ni(\mathbf{2})]ZnCl_4$ and $[Ni(\mathbf{2})](NCS)_2$ are formed by reaction of tris(1,2-diaminopropane)nickel(II) chloride with acetone, methanol, and zinc chloride at 100° in a sealed tube,[4] and of di-isothiocyanatobis(1,2-diaminopropane)nickel(II) with acetone under reflux.[5]

Bis(diaminoethane)nickel(II) perchlorate in acetone solution reacts over a period of hours at room temperature to yield the bis-complex of the tridentate β-amino-ketone $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$, $[Ni(\mathbf{3})]^{2+}$ considered to be formed by an aldol type reaction between a co-ordinated *N*-isopropylidene imino-group and an acetone molecule.[1] A solution of bis(1,2-diaminopropane)nickel(II) perchlorate [or the di-aquo,bis(methyl cyanide) or bis(pyridine) adducts], reacts similarly, but somewhat more slowly, to yield a blue, triplet

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† Unless otherwise specified, 1,2-diaminopropane represents the racemate.

‡ Other poorly co-ordinating anions which confer solubility in acetone, *e.g.* fluoroborate or hexafluorophosphate, may generally be substituted for the perchlorate ion in the reactions described in this paper.

[1] Part I, N. F. Curtis, *J.C.S. Dalton*, 1972, 1357.

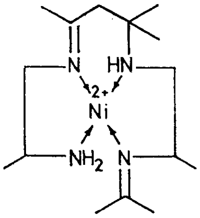
[2] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

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

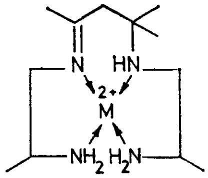
[4] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 1331.

[5] N. F. Curtis, unpublished observations.

ground state, product [Ni(**4**)](ClO_4)$_2$. This has chemical and physical properties (Experimental section) similar to those of [Ni(**3**)]$^{2+}$ and is formulated analogously as a bis-β-amino-ketone complex. In pyridine [Ni(**3**)](ClO_4)$_2$ forms a violet solution which slowly changes colour to orange as the macrocyclic complex [Ni(**5**)]$^{2+}$ is formed.[1] [Ni(**4**)](ClO_4)$_2$ reacts similarly, but more slowly, to form the macrocyclic complex *C-meso*-[Ni(**6**)](ClO_4)$_2$, none of the *C-rac* isomer being formed.[2,6,7] The conversion of [Ni(**4**)]$^{2+}$ to [Ni(**6**)]$^{2+}$ in pyridine indicates that the diaminopropane residue methyl groups are adjacent to the primary amino-groups of [Ni(**4**)]$^{2+}$, *i.e.* that the β-amino-ketone has the structure $NH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}NH{\cdot}C(CH_3)_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$. The exclusive formation of the *C-meso* isomer of [Ni(**6**)]$^{2+}$ suggests that [Ni(**4**)]$^{2+}$ has the *C-meso* configuration and that the cyclisation in pyridine is intramolecular. The *d–d* spectrum of triplet ground state [Ni(**4**)]$^{2+}$ shows three bands, which for the NiN_4O_2 chromophore suggests that the keto-groups are in *cis*-sites as for [Ni(**3**)]$^{2+}$. Adoption of the facial configuration shown for [Ni(**4**)]$^{2+}$ would explain the resistance to cyclisation, except in strong donor solvents such as pyridine, where presumably, the keto-groups are displaced from co-ordination.

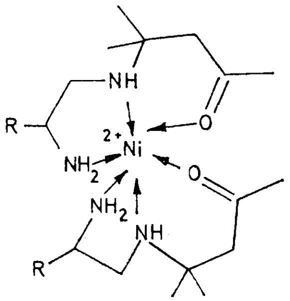


[Ni(**1**)]$^{2+}$



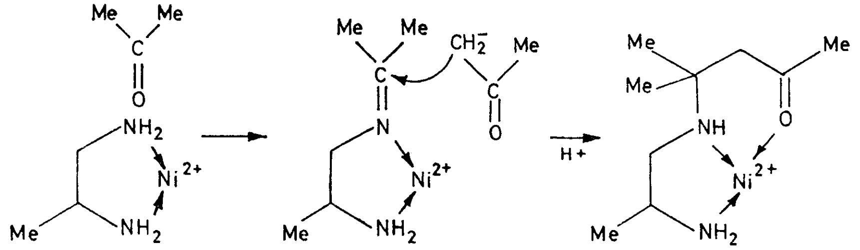
[M(**2**)]$^{2+}$

The sites of the diaminopropane residue methyl groups for (**1**) and (**2**) have not been established, although a singlet resonance for these methyl groups in the ^{1}H n.m.r. spectrum supports the structure shown for [Ni(**2**)]$^{2+}$ (T. E. McDermott and D. H. Busch, *J. Amer. Chem. Soc.*, 1967, **89**, 5780). The site of the *N*-isopropylidene group of [Ni(**1**)]$^{2+}$, *cis* or *trans* with respect to the other imino-groups is also uncertain.



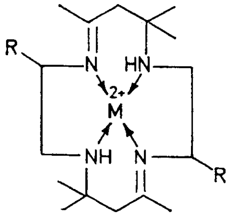
[Ni(**3**)]$^{2+}$, R = H
[Ni(**4**)]$^{2+}$, R = Me

The complex of the *R* (*l*) enantiomorph of the diamine, bis(*R*-1,2-diaminopropane)nickel(II) perchlorate, reacts in acetone similarly to the complex of the racemic diamine, to yield a product *RR*-[Ni(**4**)]$^{2+}$ which has chemical and physical properties similar to those of *RS*-[Ni(**4**)]$^{2+}$ formed from the racemic diamine, except that in pyridine it is converted exclusively to the *RR* enantiomorph of the yellow *C*-racemate of [Ni(**6**)]$^{2+}$.



SCHEME

Tris(1,2-*diaminopropane*)*nickel*(II)-*Acetone Reaction*.—A solution of tris(1,2-diaminopropane)nickel(II) perchlorate in acetone reacts over a period of days at room temperature, more rapidly under reflux, to yield ' yellow ' and ' orange ' products in approximately equal amounts,[3] since identified as the *C-rac-* and *C-meso*-isomers respectively, of the macrocyclic complex [Ni(**6**)]$^{2+}$.[*] The tris-diaminenickel(II) complexes of the enantiomorphs of 1,2-diaminopropane react with acetone to yield the *RR* and *SS* enantiomorphs of *C-rac*-[Ni(**6**)]$^{2+}$,[3] the reaction for the *R* enantiomorph (at least) giving an intermediate crystalline product [Ni(*RR*-**1**)(*R*-pn)](ClO_4)$_2$, from which [Ni(*RR*-**1**)](ClO_4)$_2$,H_2O was prepared.[8]



[M(**5**)]$^{2+}$, R = H
[M(**6**)], R = Me

The orange *C-meso* isomer of [Ni(**6**)]$^{2+}$ can be pre-

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[*] The structure of yellow *C-rac*-[Ni(**6**)](ClO_4)$_2$ has been established by *X*-ray crystallography, while the centrosymmetric space group of the orange isomer perchlorate is compatible with the *C-meso*-[Ni(**6**)](ClO_4)$_2$ formulation, as is the ^{1}H n.m.r. spectrum.[6,7]

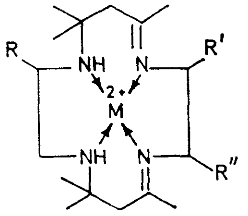
[6] N. F. Curtis, D. A. Swann, T. N. Waters, and I. E. Maxwell, *J. Amer. Chem. Soc.*, 1969, **91**, 4588.

[7] D. A. Swann, T. N. Waters, and N. F. Curtis, *J.C.S. Dalton*, 1972, 1115.

[8] H. Ito and J. Fujita, *Bull. Chem. Soc. Japan*, 1971, **44**, 741.

pared free of the yellow *C-rac* isomer by the reaction of a nickel salt with *RS*-[H$_2$(**6**)](ClO$_4$)$_2$ (below), or *via* *RS*-[Ni(**4**)](ClO$_4$)$_2$ (above). The yellow *C*-racemate has not been prepared separately, although the enantiomers can be prepared as above, or *via RR*- (and presumably also *SS*-) [Ni(**4**)]$^{2+}$.

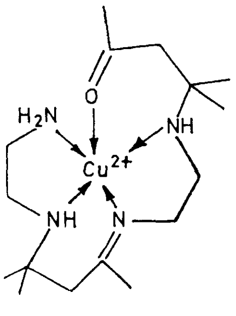
When tris(diaminoethane)nickel(II) perchlorate reacts with acetone at room temperature a mixture of the isomeric 4,11-diene, [Ni(**5**)]$^{2+}$, and 4,14-diene, [Ni(**7**)]$^{2+}$, compounds are formed, and the latter became the main product for the reaction of the nitrate salt.[1,9] There was no indication of the formation of any 4,14-diene complexes, [Ni(**8**)]$^{2+}$ or [Ni(**9**)]$^{2+}$ when tris(1,2-diaminopropane)nickel salts, including the nitrate, reacted with acetone.



[M(**7**)]$^{2+}$, R = R' = R'' = H
[M(**8**)]$^{2+}$, R = R' = Me, R'' = H
[M(**9**)]$^{2+}$, R = R'' = Me, R' = H

Bis(1,2-*diaminopropane*)*copper*(II)-*Acetone Reaction*.—The reaction of bis(1,2-diaminopropane)copper(II) perchlorate with acetone at 110°, in the presence of diaminopropane and pyridine as catalysts, to yield initially the cation [Cu(**2**)]$^{2+}$, and finally in low yield a macrocyclic complex, shown below to be *C-meso*-[Cu(**6**)]$^{2+}$, has been reported.[10]

A solution of bis(diaminoethane)copper(II) perchlorate in acetone changes in colour from magenta to blue over a period of days at room temperature (or more rapidly under reflux), and from the resultant solution the relatively stable complex of the pentadentate β-amino-ketone [Cu(**10**)]$^{2+}$ was isolated.[1] Similar colour changes occurred for a solution of bis(1,2-diaminopropane)-copper(II) perchlorate in acetone, but only starting material could be isolated from the solution. It seems likely that the colour change is due to the formation of readily hydrolysed *N*-isopropylidene *imino*-groups, but that the aldol type reaction which forms the more stable β-amino-ketone is in some way inhibited, or possibly the alternative aldol type reaction which yields the α-amino-alcohol is favoured.[1] It is not at all obvious why this reaction should not occur for the 1,2-diaminopropane copper(II) system, when it occurs readily for the 1,2-diaminopropane nickel(II) system (above), and for the diaminoethane copper(II) system (to yield [Cu(**10**)]$^{2+}$).[1] Similar behaviour occurs with diaminoethane and ethyl methyl ketone, the bis-nickel(II) complex reacting to yield an analogue of [Ni(**4**)]$^{2+}$ while for the bis-copper(II) complex, colour changes occur, but no product was isolated.[5]



[Cu(**10**)]$^{2+}$

Tris(1,2-*diaminopropane*)*copper*(II)-*Acetone Reaction*.—A solution of tris(1,2-diaminopropane)copper(II) perchlorate in acetone reacts over a period of days at room temperature to form magenta coloured [Cu(**2**)]$^{2+}$. (This is a more convenient preparation for [Cu(**2**)](ClO$_4$)$_2$ than the previously reported[2] sealed tube reaction.) When the solution was allowed to stand for a period of weeks, it slowly darkened. From this solution red and orange coloured isomeric products were isolated.* The red product is the same as the compound formed by the sealed tube reaction at 110°,[2] and also formed from *C-meso*-[H$_2$(**6**)](ClO$_4$)$_2$ (below) and hence is assigned the structure *C-meso*-[Cu(**6**)]$^{2+}$. The orange product, [Cu(**11**)]$^{2+}$, could be the *C-rac* isomer of [Cu(**6**)]$^{2+}$, or one of the isomeric 4,14-diene compounds [Cu(**8**)]$^{2+}$ or [Cu(**9**)]$^{2+}$. The relative yields of the red and orange products were dependent on the reaction conditions. Thus when a solution of tris(1,2-diaminopropane)-copper(II) perchlorate in acetone was refluxed for several days, only the red product *C-meso*-[Cu(**6**)]$^{2+}$ was isolated, as for the sealed tube reaction at 110°. At room temperature in the presence of the dehydrating agent 2,2-dimethoxypropane, the orange compound [Cu(**11**)]$^{2+}$ became the predominant product. When bis(1,2-diaminopropane)copper(II) nitrate plus 1 mol of 1,2-diaminopropane was allowed to react with acetone at room temperature (it is virtually insoluble, and was left for 2 years), only the red product was isolated. For the reaction of tris(1,2-diaminopropane)nickel(II) with acetone, approximately equal amounts of *C-meso*, and *C-rac*-[Ni(**6**)]$^{2+}$ were formed under all conditions studied, from room temperature to at least 120°, and with a range of anions and reaction conditions. Thus the isomers of [Ni(**6**)]$^{2+}$ would appear to be formed by a non-stereospecific reaction, while if the red and orange products were the *C-rac* and *C-meso* isomers of [Cu(**6**)]$^{2+}$, they would have to be formed by independent, stereospecific mechanisms.

When tris(diaminoethane)-copper(II), or -nickel(II), reacted with acetone, the 4,11-diene, [M(**5**)]$^{2+}$, and 4,14-diene, [M(**7**)]$^{2+}$, compounds are formed with a dependence of relative yield on reaction conditions[1,9]

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* The space group and unit cell dimensions of the orange product have been reported.[6]

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

[10] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1962, 3016.

similar to that of the tris(diaminopropane)copper(II)–acetone products *C-meso*-[Cu(**6**)]$^{2+}$ and [Cu(**11**)]$^{2+}$. Moreover, the reaction of the diaminoethane analogue of [Cu(**2**)]$^{2+}$ with acetone in the presence of 1 mol of diaminoethane yields [Cu(**7**)]$^{2+}$, a situation analogous to that present in the solution of tris(1,2-diaminopropane)copper(II) perchlorate in acetone after a few days. However, both the reaction yielding the *RS*-[Cu(**6**)]$^{2+}$ and the [Cu(**11**)]$^{2+}$ (*i.e.* [Cu(**8**)]$^{2+}$ or [Cu(**9**)]$^{2+}$) ions would have to be stereospecific, which also appears unlikely.

The different characteristics of the reaction of tris-(1,2-diaminoethane) complexes of nickel(II) and copper-(II), with acetone are presumably related to the observed differences in the reactivity of the bis-complexes with acetone.

1,2-*Diaminopropane–Acetone Reaction.*—It was observed that when copper(II) was added to a solution of diaminoethane in acetone which had been allowed to react for *ca.* 8 days at room temperature, or 8 h under reflux, the complex [Cu(**10**)]$^{2+}$ was formed.[1] A solution of 1,2-diaminopropane in acetone slowly darkened on standing or refluxing. When copper perchlorate (Cu : en = 1 : 2) was added to the solution, a deep blue colour formed. Addition of propan-2-ol caused deposition of a deep green gum, but on standing this redissolved and bis(1,2-diaminopropane)copper(II) perchlorate crystallised. When nickel perchlorate (Ni : pn = 1 : 2) was added to the amine–acetone solution a gelatinous precipitate formed. On standing this slowly became dark and tarry, but no acid stable nickel complex could be isolated at any stage. For the equivalent reaction with diaminoethane, a similar gelatinous precipitate formed, but [Ni(**5**)](ClO$_4$)$_2$ slowly crystallised.

1,2-*Diaminopropane Hydroperchlorate–Acetone Reaction.*—1,2-Diaminopropane-mono-hydroperchlorate reacts with acetone, diacetone alcohol, or mesityl oxide to yield crystalline [H$_2$(**6**)](ClO$_4$)$_2$, identified as the *C-meso* isomer by conversion to *C-meso*-[Ni(**6**)](ClO$_4$)$_2$.[6,11] The exclusive formation of the *C-meso* isomer is apparently a solubility effect, since no product was isolated when the reaction was attempted using the *R*-diamine.

EXPERIMENTAL

Caution.—Perchlorate salts of many of these compounds are explosive. In general they have not been found to be shock sensitive, but may detonate on heating above *ca.* 150°. Particular caution should be exercised with [M(pn)$_2$](ClO$_4$)$_2$ and [H$_2$(pn)](ClO$_4$)$_2$, which detonate violently. The compounds [Ni(**4**)](ClO$_4$)$_2$, [M(**6**)](ClO$_4$)$_2$, and [H$_2$(**6**)](ClO$_4$)$_2$ decompose non-violently when heated (M = Ni^{II} or Cu^{II}).

RS-*Bis*(7-*amino*-4,4-*dimethyl*-5-*azaoctan*-2-*one*)*nickel*(II) *Perchlorate*, *RS*-[Ni(**4**)](ClO$_4$)$_2$.—A solution of bis(1,2-diaminopropane)nickel(II) perchlorate, or the di-aquo, bis-pyridine, or bis(methyl cyanide) adducts, (10 g) in acetone (100 ml) was allowed to stand at room temperature for *ca.* 1 week. The acetone was removed using a rotary evaporator and the residue recrystallised from hot ethanol as blue-violet feathery *crystals*. Yield 90% (Found: C, 36·2; H, 6·8; Ni, 9·5. $C_{18}H_{40}Cl_2N_4NiO_{10}$ requires C, 35·9; H, 6·7; Ni, 9·8%). Magnetic susceptibility: $10^3 \chi_g$ (293·6 K) = 3970, μ_{eff} = 3·14 B.M., corrected for diamagnetism and T.I.P. The compound also crystallised as a hydrate from methanol–water.

RR-*Bis*(7-*amino*-4,4-*dimethyl*-5-*azaoctan*-2-*one*)*nickel*(II) *Perchlorate*, *RR*-[Ni(**4**)](ClO$_4$)$_2$.—As for the previous preparation, using *R*-1,2-diaminopropane (Found: C, 35·6; H, 6·8; Ni, 9·4. $C_{18}H_{40}Cl_2N_4NiO_{10}$ requires C, 35·9; H, 6·7; N, 9·3%).

'*Orange*' *Perchlorate*, [Cu(**11**)](ClO$_4$)$_2$, *probably* C-rac-(3,5,7,7,10,12,14,14-*Octamethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Perchlorate*, *C-rac*-[Cu)(**6**](ClO$_4$)$_2$.—A solution of tris(1,2-diaminopropane)copper(II) perchlorate (10 g) in acetone (200 ml), conveniently prepared by the addition of 1 mol of 1,2-diaminopropane to a solution of the bis complex, plus 2,2-dimethoxypropane (5 ml) was allowed to stand at room temperature. The solution changed from blue to magenta in colour, and after several days [Cu(**2**)](ClO$_4$)$_2$ could be isolated in high yield. On further standing the solution slowly became dark and tarry. After *ca.* 5 weeks the solution was evaporated to dryness using a rotary evaporator, and the residue boiled with ethyl acetate. After standing for several hours at room temperature the liquid was decanted and the residue recrystallised from hot dilute perchloric acid. The 'orange perperchlorate' was separated from the smaller amount of red *C-meso*-[Cu(**6**)](ClO$_4$)$_2$ by several recrystallisations from hot dilute perchloric acid (Found for orange salt: C, 37·9; H, 6·3; Cu, 9·8. $C_{18}H_{36}Cl_2CuN_4O_8$ requires C, 37·9; H, 6·4; Cu, 9·8%).

I.r. Spectra.—*RS*-[Ni(**4**)](ClO$_4$)$_2$,H$_2$O: ν(OH), 3510m,br; ν(NH), 3325s, 3270m, 3240m, 3230w, and 3140vw; ν(C:N), 1680s; δ(HOH), *ca.* 1640sh; δ(NH$_2$), 1585m cm^{-1}. *RR*-[Ni(**4**)](ClO$_4$)$_2$: ν(NH), 3327s, 3275m, and 3248s,sp; ν(C:N), 1683s; δ(NH$_2$), 1592m cm^{-1}.

C-rac-[Cu(**6**)](ClO$_4$)$_2$: ν(NH), 3227s; ν(C:N), 1663s cm^{-1}.

d–d *Spectra.*—*RS*[Ni(**4**)](ClO$_4$)$_2$, 10 500, 18 000, 28 800 cm^{-1}. *RR*-[Ni(**4**)](ClO$_4$)$_2$, 10 600, 18 000, 28 500 cm^{-1}, by reflectance, spectra not appreciably different in methanol.

C-rac-[Cu(**6**)](ClO$_4$)$_2$ in water, 19 300 cm^{-1}, ε = 105 mol^{-1} cm^{-1}. The colour of the solution varies from pink in acetone (20 350 cm^{-1}) through violet in water to blue in dimethylformamide or aqueous ammonia, as observed for the *C-meso* isomer and related compounds. Similar effects are commonly observed for square planar copper(II) compounds and are attributed to solvent interactions in the tetragonal co-ordination sites.

[2/1767 *Received, 28th July,* 1972]

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[11] D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, 1971, **10**, 1739.