Some Metal-ion Complexes with Ligands formed by Reaction of Amines with Aliphatic Carbonyl Compounds. Part III.[1] Some Compounds formed by Reaction of 1,3-Diaminopropane Nickel(II) Compounds with Acetone

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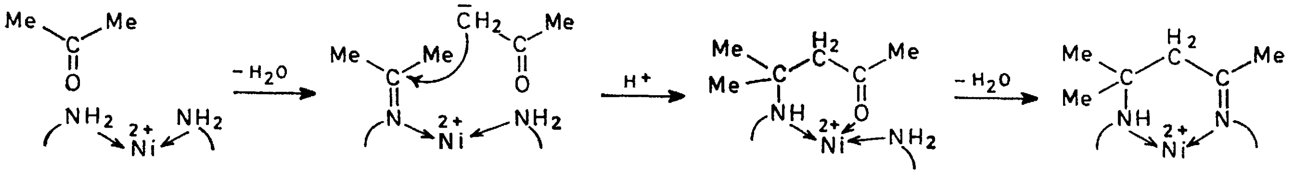
Bis(1,3-diaminopropane)nickel(II) salts react with acetone to give bisisopropylideneamino-complexes, as singlet ground state salts for ClO_4^- and BF_4^-, or as triplet ground state di-acido-derivatives for NO_3^-, NCS^-, or Cl^-. In the presence of a third mol of the diamine reaction continues to yield salts of a cation with a tetradentate ligand formed from two diamine residues linked by an ' amine-imine bridge ' derived from two acetone residues, and with an additional isopropylideneamino group. Reaction continues, the final product having a tetra-azacyclohexadecadiene ligand formed from two diamine residues linked by two such bridges. For the nitrate, an intermediate triplet ground state compound with a pentadentate β-aminoketone ligand and one co-ordinated nitrato-group was isolated.

PREVIOUS papers in this series have reported reactions of diaminoethane [2] and 1,2-diaminopropane [1] complexes of nickel(II) and copper(II) with acetone. These reactions yield a variety of products with ligands incorporating amine and acetone residues.[3] The initial product of the reaction was considered to be an isopropylideneamine (not isolated), which undergoes an aldol type reaction between the imino-group and an acetone molecule to yield a β-aminoketone. This may be stabilised by co-ordination of the keto-group, or may undergo an imine formation reaction with a primary amino-group to yield a compound with a ligand which has two amine residues linked by a three carbon atom ' amine-imine bridge '. (See Scheme). Formation of two such bridges for diamines results in a tetra-aza macrocyclic complex.



SCHEME

Tris(1,3-diaminopropane)nickel(II) perchlorate reacts rapidly with acetone to yield the bis(isopropylideneamino)compound $[Ni(\mathbf{1})_2](ClO_4)_2$, which crystallised after *ca.* 30 min at room temperature.[4] When the reaction was allowed to continue for several days, the compound $[Ni(\mathbf{2})](ClO_4)_2$ with a tetra-aza macrocyclic ligand was formed.[4] At an intermediate stage of this reaction the compound $[Ni(\mathbf{3})](ClO_4)_2$, isolated as an ethanolate, was obtained.[5] The *N*-isopropylidene group of (**3**) was slowly hydrolysed off in boiling water to yield $[Ni(\mathbf{4})](ClO_4)_2$.[5]

The compound $[Ni(\mathbf{4})](ClO_4)_2$ was obtained when tris(1,3-diaminopropane)nickel(II) perchlorate was refluxed in mesityl oxide–methanol,[6] and $[Ni(\mathbf{2})](ClO_4)_2$ when it was refluxed in mesityl oxide.[5,6] Reactions of some bis(1,3-diaminopropane)- and some other tris(1,3-diaminopropane)-nickel(II) salts with acetone are here reported.

The reactions of (1,3-diaminopropane)nickel(II) complexes with acetone differ in many respects from those of the analogous diaminoethane complexes. Bis(di-

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[1] Part II, N. F. Curtis, *J.C.S. Dalton*, 1973, 863.

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

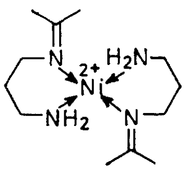
[3] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

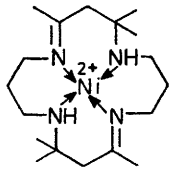
[4] D. A. House and N. F. Curtis, *J. Amer. Chem. Soc.*, 1964, **86**, 223.

[5] H. K. J. Powell and M. E. Rumble, personal communication, M. E. Rumble, Thesis, University of Canterbury, 1969.

[6] D. St. C. Black and H. Greenland, *Austral. J. Chem.*, 1972, **25**, 1315.

aminoethane)nickel(II) perchlorate reacts with acetone at room temperature to yield the bis(β-aminoketo) cation $[\mathrm{Ni}(\mathbf{6})_2]^{2+}$. For the bispyridine adduct, and for the chloro-, nitrato- and isothiocyanato-compounds, reaction continues, to yield $[\mathrm{Ni}(\mathbf{5})]^{2+}$, the diaminoethane analogue of $[\mathrm{Ni}(\mathbf{3})]^{2+}$, apparently because these ligands prevent stabilisation of the β-amino-ketone by co-ordination of the keto-group, and hence facilitate the imine formation reaction.[2] Tris(diaminoethane)nickel(II) perchlorate reacts with acetone to yield a mixture of the isomeric 4,11- and 4,14-diene macrocyclic complexes, $[\mathrm{Ni}(\mathbf{7})]^{2+}$ and $[\mathrm{Ni}(\mathbf{8})]^{2+}$.[2,7] The cation $[\mathrm{Ni}(\mathbf{5})]^{2+}$ has been isolated from the reacting solution and appears to be a precursor of $[\mathrm{Ni}(\mathbf{8})]^{2+}$. The trisamino nitrate salt reacts slowly to yield only $[\mathrm{Ni}(\mathbf{8})]^{2+}$.[2]


$[\mathrm{Ni}(\mathbf{1})_2]^{2+}$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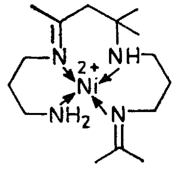
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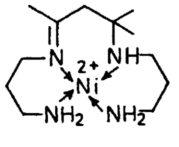
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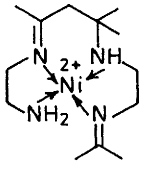
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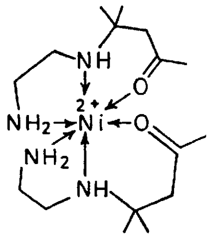
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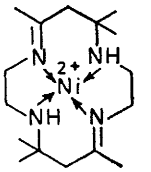
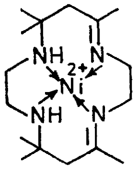
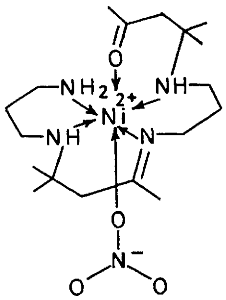

$[\mathrm{Ni}(\mathbf{7})]^{2+}$


$[\mathrm{Ni}(\mathbf{8})]^{2+}$


$[\mathrm{Ni}(\mathbf{9})\mathrm{NO}_3]^{+}$

Reactions of Bis(1,3-*diaminopropane*)*nickel*(II) *Compounds with Acetone.*—Bis(1,3-diaminopropane)nickel(II) compounds react rapidly with acetone to form the di-imine cation $[\mathrm{Ni}(\mathbf{1})_2]^{2+}$. The singlet ground state perchlorate and fluoroborate salts and the triplet ground state di-isothiocyanato-compound crystallise from the solution but the dinitrato- and dichloro-compounds are more soluble. The dinitrato-compound has an i.r. spectrum * indicative of unidentate co-ordinated nitrate and shows the four band *d–d* reflectance spectrum compatible with *trans*-geometry for the $\mathrm{NiN_4O_2}$ chromophore. All the compounds are hydrolysed rapidly by dilute mineral acid, yielding acetone as the only carbonyl product. None of the compounds reacts further with acetone to yield identifiable products, although very slow polymerisation of the acetone occurs with prolonged reaction.

Reaction of Tris(1,3-*diaminopropane*)*nickel*(II) *Salts with Acetone.*—Tris(1,3-diaminopropane)nickel(II) salts with a variety of anions were allowed to react with acetone at room temperature. For the perchlorate, fluoroborate, and thiocyanate the di-imine compounds crystallised after *ca.* 30 min. For the chloride and nitrate the di-imine compounds were soluble, but were isolated from the solutions after *ca.* 24 h. When reaction was allowed to continue, the perchlorate and fluoroborate of $[\mathrm{Ni}(\mathbf{1})_2]^{2+}$ slowly dissolved, and all the solutions turned yellow over 2—3 days. For the nitrate, bromide, and iodide, yellow singlet ground state salts crystallised and analogous, but more soluble, perchlorate and fluoroborate salts could be isolated. These all analysed for, and had spectroscopic properties expected of, salts of $[\mathrm{Ni}(\mathbf{3})]^{2+}$. They were hydrolysed by dilute mineral acid to yield both acetone and mesityl oxide, as for the diaminoethane analogue $[\mathrm{Ni}(\mathbf{5})]^{2+}$. If the reactions were allowed to continue, the solids redissolved, and salts of the macrocyclic complex $[\mathrm{Ni}(\mathbf{2})]^{2+}$ ultimately crystallised.

For the nitrate, as the yellow $[\mathrm{Ni}(\mathbf{3})](\mathrm{NO_3})_2$ dissolved, a pink product crystallised over a period of days. After a few more days, red crystals of $[\mathrm{Ni}(\mathbf{2})](\mathrm{NO_3})_2$ formed, and increased in amount at the expense of the pink material. The properties of this pink material show that it is a distinct compound, although variable analytical results indicate that samples were usually impure. Since the reaction starts with sparingly soluble tris(1,3-diaminopropane)nitrate and proceeds *via* sparingly soluble $[\mathrm{Ni}(\mathbf{3})](\mathrm{NO_3})_2$, and the pink product, ultimately to sparingly soluble $[\mathrm{Ni}(\mathbf{2})](\mathrm{NO_3})_2$, contamination is not surprising. The same compound is formed when $[\mathrm{Ni}(\mathbf{3})](\mathrm{NO_3})_2$ is reacted with acetone in the presence of 1,3-diaminopropane. The $[\mathrm{Ni}(\mathbf{3})]^{2+}$ salts do not react further with acetone in the absence of the diamine, even in the presence of bases such as diethylamine. Samples of the pink compound had magnetic susceptibilities in the range expected for triplet ground state, pseudo-octahedral nickel(II), although $[\mathrm{Ni}(\mathbf{2})](\mathrm{NO_3})_2$ and $[\mathrm{Ni}(\mathbf{3})](\mathrm{NO_3})_2$ are both diamagnetic. The material was hydrolysed rapidly by dilute mineral acid, showing that the ligand was not cyclic, and yielding mesityl oxide as the only carbonyl product, showing that the acetone was present as dimeric units. The compound was insoluble in most solvents, and when soluble was converted to $[\mathrm{Ni}(\mathbf{2})](\mathrm{NO_3})_2$, slowly in methanol, more rapidly in methanol containing pyridine, or in dimethyl sulphoxide; thus recrystallisation did not improve the purity. The i.r. spectrum shows bands assignable to both primary

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* Spectroscopic and magnetic susceptibility data are included in the Experimental section.

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

and secondary amino-groups, two bands in the ' carbonyl ' region [νC=N and ν(C=O)], and bands assignable to both unidentate co-ordinated and ionic nitrate. The reflectance spectrum is compatible with a *trans*-NiN_4O_2 chromophore, and the compound is assigned the structure [Ni(**9**)NO_3]NO_3, with a linear pentadentate β-aminoketo-ligand and with the keto- and nitrato-oxygen donor atoms *trans*. The compound [Cu(**10**)]$(ClO_4)_2$, with a ligand similar to (**9**) is formed by reaction of bis(diaminoethane)copper(II) perchlorate with acetone, and this has similar hydrolysis properties and is cyclised under similar conditions.[2] The ligands (**9**) and (**10**) are stabilised by co-ordination of the keto-group, but in donor solvents this group is displaced, and cyclisation by intramolecular imine formation occurs rapidly. The isolation of the nitrato-nitrate derivative of $[Ni(\mathbf{9})]^{2+}$ appears to be the result of a fortuitous combination of the ligand properties of the nitrate ion and low solubility of the resultant nitrate salt, but analogous compounds probably occur as intermediates for salts with other anions.

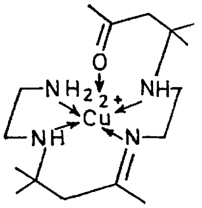
The nitrate salt of the macrocyclic cation is converted by metathesis into the previously reported perchlorate salt of $[Ni(\mathbf{2})]^{2+}$.

Tris(1,3-diaminopropane)nickel(II) salts with other anions react similarly to the perchlorate, yielding the same $[Ni(\mathbf{2})]^{+}$ cation. The thiocyanate reacts exceedingly sluggishly beyond the $Ni(\mathbf{1})_2(NCS)_2$ stage, but eventually forms the previously reported[4] dithiocyanato-derivative of $[Ni(\mathbf{2})]^{2+}$.

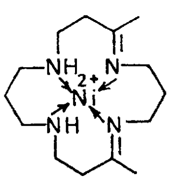
Reactions of 1,3-*Diaminopropane with Acetone*.—When nickel(II) salts were added to solutions of 1,3-diaminopropane in acetone which had been allowed to react for varying periods in Ni^{2+} : amine ratios of 1 : 2 or 1 : 3, derivatives of $[Ni(\mathbf{1})_2]^{2+}$ were formed. When 1,3-diaminopropane mono-hydroperchlorate was reacted with acetone, polymerisation of the acetone occurred, but no crystalline product was obtained, directly or by precipitation with various solvents. These results may be compared with the reactions of acetone with diaminoethane under similar conditions.[2]

Stereochemistry of the Compounds and Reaction Mechanism.—Discussion of the stereochemistry of the reactions and products is inhibited by the fact the structures have not been established for any of the compounds formed by reaction of 1,3-diaminopropane complexes with acetone. Barefield and Busch deduced from the ^1H n.m.r. spectrum of the tetra-imine formed by nitric acid oxidation of $[Ni(\mathbf{2})]^{2+}$ that (**2**) has the 1,9-diene structure, *i.e.* as represented, with the pairs of amino and imino donor groups *trans*.[8] However, the related cation $[Ni(\mathbf{11})]^{2+}$, formed by reaction of methyl vinyl ketone and 1,3-diaminopropane in the presence of a nickel(II) salt has the 1,12-diene structure,[9] so the 1,12-diene structure $[Ni(\mathbf{12})]^{2+}$ cannot be excluded.

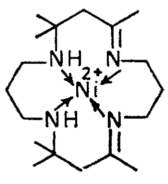
The first isolated product of the reaction of bis- or tris-(1,3-diaminopropane)nickel(II) salts with acetone is the di-*N*-isopropylidene compound $[Ni(\mathbf{1})_2]^{2+}$. *N*-Isopropylidene compounds are postulated as the initial product for the reactions of 1,2-diamine complexes also, but these compounds were not isolated as they react further with acetone.[1,2] The low solubility of the di-imine compounds as perchlorates applies to the derivatives of a wide variety of aldehydes and ketones, which crystallise when bis- or tris-(1,3-diaminopropane)nickel(II) perchlorates react with the carbonyl compound, or with a methanolic solution of the carbonyl compound. Analogous compounds do not crystallise for diaminoethane.



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



$[Ni(\mathbf{11})]^{2+}$



$[Ni(\mathbf{12})]^{2+}$

The stereochemistry of $[Ni(\mathbf{1})_2]^{2+}$ has not been established, except that for the square planar cation, the imino-groups cannot be adjacent. They could be *cis* on the same diamine residue, or *trans* on separate diamine residues. $[Ni(\mathbf{1})_2](ClO_4)_2$ does not react with acetone, even in the presence of bases such as diethylamine. It does react, in the presence of 1,3-diaminopropane, to yield $[Ni(\mathbf{3})]^{2+}$. The function of the diamine could be stereochemical, the reacting species having three co-ordinated diamines, and hence having the elements of $[Ni(\mathbf{1})_2]^{2+}$ in *cis*-co-ordination. However, the possibility that the aldol-type reaction occurs for the ' free ' diamine, which then co-ordinates and undergoes an imine condensation to yield $[Ni(\mathbf{3})]^{2+}$ cannot be excluded.

EXPERIMENTAL

trans-*Dinitratobis*(2-*methyl*-6-*amino*-3-*azahex*-2-*ene*)*nickel*-(II), *trans*-$Ni(\mathbf{1})_2(NO_3)_2$.—Tris(1,3-diaminopropane)nickel-(II) nitrate (3 g) was stirred with acetone (150 ml) for 4 h. The solution was filtered from unreacted starting material, evaporated to a small volume, and the pale blue product precipitated by the addition of ether (Found: C, 29·9; H, 7·3; Ni, 12·7. $C_{12}H_{28}N_6NiO_6$ requires C, 30·7; H, 7·3; Ni, 12·5%).

trans-*di-isothiocyanatobis*(2-*methyl*-6-*amino*-3-*azahex*-2-*ene*)*nickel*(II), *trans*-$Ni(\mathbf{1})_2(NCS)_2$.—Dithiocyanatobis(1,3-diaminopropane)nickel(II), (3 g) was refluxed in acetone (100 ml) for 6 h, then evaporated to *ca*. 20 ml. The purple crystals of the product were filtered from the cold solution and recrystallised from hot methanol (Found: C, 42·0; H, 7·5; Ni, 14·5. $C_{14}H_{28}N_6NiS_2$ requires C, 41·7; H, 7·0; Ni, 14·5%).

(2,8,8,10-*Tetramethyl*-14-*amino*-3,7,11-*triazatetradeca*-2,10-*diene*)*nickel*(II) *Nitrate Hydrate*, $[Ni(\mathbf{3})](NO_3)_2,H_2O$.—Tris-(1,3-diaminopropane)nickel(II) nitrate (6 g) was stirred in acetone (150 ml) for 24 h. The yellow crystalline product which separated in *ca*. 70% yield as the starting material

[8] E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 108.

[9] J. F. Meyers and C. H. L. Kennard, *Chem. Comm.*, 1972, 77.

dissolved was filtered off and washed with ethanol. Further product was obtained by adding propan-2-ol to the filtrate and reducing the volume using a rotary evaporator. The *product* was recrystallised by dissolving in hot methanol, adding propan-2-ol, and reducing the volume (Found: C, 38·3; H, 7·3; Ni, 12·4. $C_{15}H_{34}N_6NiO_7$ requires C, 38·4; H, 7·3; Ni, 12·5%).

The yellow bromide hemihydrate and iodide salts of $[\mathrm{Ni}(\mathbf{3})]^{2+}$ were prepared and recrystallised similarly starting with the bromide and iodide of tris(1,3-diaminopropane)-nickel(II) and stirring for *ca.* 2 and 4 days respectively (Found for $[\mathrm{Ni}(\mathbf{3})]\mathrm{Br_2,0{\cdot}5H_2O}$: C, 35·9; H, 6·7; Ni, 11·9. $C_{30}H_{66}Br_4N_8Ni_2O$ requires C, 36·3; H, 6·7; Ni, 11·8%. Found for $[\mathrm{Ni}(\mathbf{3})]\mathrm{I_2}$: C, 31·3; H, 5·6; Ni, 10·2. $C_{15}H_{32}I_2$-Ni_4Ni requires C, 31·0; H, 5·6; Ni, 10·1%).

Spectroscopic and Magnetic Data.—$\mathrm{Ni}(\mathbf{1})_2(\mathrm{NO_3})_2$ i.r.: $\nu(\mathrm{NH_2})$: 3275, 3325, 3375; $\delta(\mathrm{NH_2})$: 1595, 1612; $\nu(\mathrm{C{:}N})$: 1646; unidentate $\mathrm{NO_3}^-$: ν_2: 816; ν_3: 1296, 1418; ν_4: 706, 725; $(\nu_1 + \nu_3)$: 2315, 2440; $(\nu_1 + \nu_4)$: 1746, 1765 $\mathrm{cm^{-1}}$; *d–d* (reflectance): 26·6, 17·2, 14·1sh, $8{\cdot}2 \times 10^3$ $\mathrm{cm^{-1}}$.

$\mathrm{Ni}(\mathbf{1})_2(\mathrm{NCS})_2$ i.r.: $\nu(\mathrm{NH_2})$: 3323, 3249, 3201, 3160; $\nu(\mathrm{C{\equiv}N})$: 2087s; $\nu(\mathrm{C{=}N})$: 1676, 1662; $\delta(\mathrm{NH_2})$: 1592; $\nu(\mathrm{CS})$: 777 $\mathrm{cm^{-1}}$; $\chi_g = 9{\cdot}774 \times 10^{-6}$ (297·2 K), $\mu_{\mathrm{eff}} = 3{\cdot}07$ B.M.

$[\mathrm{Ni}(\mathbf{3})](\mathrm{NO_3})_2,\mathrm{H_2O}$ i.r.: $\nu(\mathrm{OH})$: 3535, 3460; $\nu(\mathrm{NH_2})$: 3205; $\delta(\mathrm{NH_2})$: 1612; $\nu(\mathrm{NH})$: 3137; $\nu(\mathrm{C{:}N})$: 1663; $\mathrm{NO_3}^-$: ν_2: 827; ν_3: 1353; ν_4: 705; $(\nu_1 + \nu_3)$: 2380; $(\nu_1 + \nu_4)$: 1746 $\mathrm{cm^{-1}}$; *d–d* (in dimethylformamide): $22{\cdot}4 \times 10^3$ $\mathrm{cm^{-1}}$.

$[\mathrm{Ni}(\mathbf{9})\mathrm{NO_3}]\mathrm{NO_3}$ i.r. $\nu(\mathrm{NH_2})$: 3375, 3335, 3280; $\delta(\mathrm{NH_2})$: 1607, 1591; $\nu(\mathrm{NH})$: 3140; $\nu(\mathrm{C{:}N})$: 1668; $\nu(\mathrm{C{:}O})$: 1648; unidentate $\mathrm{NO_3}^-$: ν_2: 815; ν_3: 1270, 1375; ν_4: 701?, 720; $(\nu_1 + \nu_3)$: 2320, 2415; $(\nu_1 + \nu_4)$: 1765, 1747; ionic $\mathrm{NO_3}^-$: ν_2: 815; ν_3: 1335; ν_4: 701; $(\nu_1 + \nu_3)$: 2365; $(\nu_1 + \nu_4)$: 1747 $\mathrm{cm^{-1}}$; *d–d*: 28·1, 20·4, 14·5sh, $8{\cdot}2 \times 10^3$ $\mathrm{cm^{-1}}$ {the 20,400 $\mathrm{cm^{-1}}$ band is assigned to $[\mathrm{Ni}(\mathbf{2})](\mathrm{NO_3})_2$ impurity}; $\chi_g = 7{\cdot}35 \times 10^{-6}$ (288·2 K), $\mu_{\mathrm{eff}} = 3{\cdot}0$ B.M.

[2/2612 *Received, 20th November,* 1972]