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

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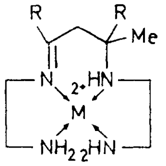
Bis(diaminoethane)nickel(II) perchlorate reacts with butanone (ethyl methyl ketone) at room temperature to yield the bis complex of the β-aminoketone $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}C(CH_3)(CH_2{\cdot}CH_3){\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_3$ which acts as a tridentate ligand. In pyridine this undergoes intramolecular imine formation to yield the nickel(II) complex of 5,7,12,14-tetraethyl-7,14-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (2). The first reaction at higher temperatures, or in the presence of co-ordinating anions (*e.g.* Cl^-, NO_3^-, NCS^-) or solvents (*e.g.* methanol, methyl cyanide, pyridine) yields the complex of the tetradentate ligand $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C(CH_2{\cdot}CH_3){\cdot}CH_2{\cdot}C(CH_3)(CH_2{\cdot}CH_3){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C(CH_3){\cdot}CH_2{\cdot}CH_3$, from which the imino group can be hydrolysed to yield the complex of the ligand $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}N{:}C(CH_2{\cdot}CH_3)CH_2{\cdot}C(CH_3)(CH_2{\cdot}CH_3){\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2$, (1). The salt $[H_2(2)](ClO_4)_2$, crystallizes when $[H(en)]ClO_4$ is reacted with butanone, and the compounds $[Ni(2)](ClO_4)_2$ and $[Cu(2)](ClO_4)_2$ were prepared by reaction of this with the metal acetates. Tris(diaminoethane)nickel(II) perchlorate reacts extremely slowly with butanone to yield the complex of 5,7,12,14-tetraethyl-7,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,14-diene (3), a geometrical isomer of (2). The large difference in the apparent rate of the last reaction compared with the equivalent reaction with acetone is discussed.

COMPOUNDS formed by reactions with acetone of diaminoethane,[2] 1,2-[3] and 1,3-diaminopropane[1] as monoprotonated salts and as nickel(II) and copper(II) complexes have been described.[4] Analogous compounds formed with diaminoethane and butanone (ethyl methyl ketone) are here described, and the reactions with the two ketones compared.

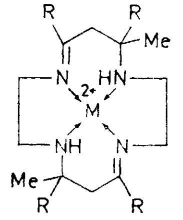
Reaction of bis(diaminoethane)copper(II) perchlorate with butanone at 110° has been reported by Blight and Curtis.[5] The cation $[Cu(1)]^{2+}$, with a linear tetradentate ligand was formed after one day, and a complex of a tetra-aza macrocycle was obtained in low yield after five days.[5] This latter product was tentatively formulated as the 4,11-diene cation $[Cu(2)]^{2+}$, but evidence, below, supports assignment of the isomeric 4,14-diene structure $[Cu(3)]^{2+}$. Blight also described a reaction of tris(diaminoethane)nickel(II) perchlorate with butanone at 110° which gave in very low yield after several weeks a product formulated as $[Ni(2)]^{2+}$,[6] but now considered to have the isomeric structure $[Ni(3)]^{2+}$. Since tris(diaminoethane)-nickel(II) and -copper(II) perchlorates react rapidly with acetone at room temperature to yield a mixture of the isomeric complexes $[M(4)]^{2+}$ and $[M(5)]^{2+}$, while reaction at higher temperature yields only $[M(4)]^{2+}$,[2] the large difference in the reaction rates for acetone and butanone, and the difference in the stereochemistry of the products have been further investigated.

Reactions of Bis(diaminoethane)nickel(II) *Compounds*.—Bis(diaminoethane)nickel(II) compounds react similarly with acetone[2] and butanone at room temperature to yield products of two types. The perchlorate and fluoroborate, and their bis adducts with weak ligands such as water, methyl cyanide, methanol, *etc.*, give the blue, triplet ground state bis complexes of tridentate β-aminoketones, $[Ni(6)_2]^{2+}$ and $[Ni(7)_2]^{2+}$.[2] The bis pyridine adducts, and the dichloro, di-isothiocyanato, and di-nitrato compounds give the yellow, singlet ground state cations $[Ni(8)]^{2+}$ and $[Ni(9)]^{2+}$, with linear, tetradentate ligands.[2] These products are also formed by the previous reactants at higher temperatures, or in the presence of appreciable amounts of donor solvents such as methanol. The initially formed bisisopropylideneamino complex is considered to undergo an aldol type reaction with the ketone to form the β-aminoketone.[2] In the absence of competitive ligands this species is



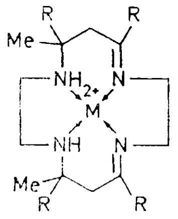
$[M(1)]^{2+}$ R = Et

$[M(8)]^{2+}$ R = Me



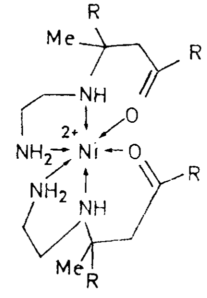
$[M(2)]^{2+}$, R = Et

$[M(4)]^{2+}$, R = Me



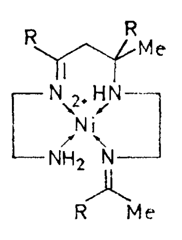
$[M(3)]^{2+}$, R = Et

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



$[Ni(6)_2]^{2+}$, R = Me

$[Ni(9)_2]^{2+}$, R = Et



$[Ni(7)]^{2+}$, R = Me

$[Ni(10)]^{2+}$, R = Et

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

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

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

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

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

[6] M. M. Blight, *Thesis, Victoria University of Wellington*, 1957.

stabilized by co-ordination of the keto group, and repetition of the aldol type reaction on the second imino group gives $[Ni(6)_2]^{2+}$ or $[Ni(7)_2]^{2+}$. In the presence of ligands which compete with the keto group for the co-ordination site on the nickel(II) ion, intra-molecular imine formation occurs to give $[Ni(8)]^{2+}$ or $[Ni(9)]^{2+}$ which do not react further with acetone, but may undergo hydrolysis of the ketimino group to give $[Ni(8)]^{2+}$ or $[Ni(1)]^{2+}$.

The reactions of bis(diaminoethane)nickel(II) compounds with acetone and butanone thus follow the same course, to yield similar products. The rate of reaction is slower with butanone by a factor of the order of 5, but the difference is insignificant compared with the large difference in the rates of reaction with the tris(diaminoethane) complex.

The β-aminoketone compound $[Ni(6)_2]^{2+}$ forms a blue solution in pyridine which turns yellow over a period of minutes as the 4,11-diene macrocyclic cation $[Ni(4)]^{2+}$ is formed.[2] The analogous compound derived from butanone, $[Ni(7)_2]^{2+}$ reacts similarly over a period of days to form a product isomeric with, and not interconvertible with, the product of the tris(diaminoethane)nickel(II) butanone reaction. This is considered (below) to have the 4,11-diene structure $[Ni(2)]^{2+}$, formed by intramolecular imine formation with $[Ni(7)_2]^{2+}$.

Reactions of Tris(diaminoethane)nickel(II) *Compounds*.—Tris(diaminoethane)nickel(II) perchlorate forms a violet solution in acetone which begins to turn yellow within minutes. Initially the reaction is reversed by water, suggesting that readily hydrolysable isopropylideneamines are present. After a period of hours, water stable but acid hydrolysable species appear in the solution, and $[Ni(8)]^{2+}$ can be isolated. Still later, the macrocycle complexes $[Ni(4)]^{2+}$ and $[Ni(5)]^{2+}$ appear in the solution, and reaction proceeds completely to these, in a ratio of *ca.* 3 : 1 over a period of days.[2,7]

Tris(diaminoethane)nickel(II) perchlorate dissolves sparingly in butanone to form a violet solution which turns brown over a period of days at room temperature, or hours under reflux. The spectrum of the solution shows that this colour arises from the tail of an intense band in the u.v., probably of ketone polymers, and not as in the acetone case, from singlet ground state NiN_4 species. After a period of days at room temperature a small amount of blue $[Ni(7)_2](ClO_4)_2$ usually crystallizes. Thereafter little change occurs in the system except that the solution slowly becomes darker with tarry ketone polymers. No further tris(diaminoethane)nickel(II) perchlorate appears to dissolve. One reaction was left for three years, when most of the tris complex remained unreacted. A minute yield of $[Ni(3)]^{2+}$ was obtained from the solution of this reaction, by treatment with acid, when all non cyclic amine species were hydrolysed or decomposed by protonation. The same product is obtained very slowly at temperatures up to 140°, again the bulk of the tris(diaminoethane)nickel(II) remaining unreacted after several months.

The large apparent difference in the rate of reaction of the tris(diaminoethane) complex with the two ketones is surprising in view of the similarity in the rate of reaction, and products obtained, for the bis(diaminoethane) complexes. The key to the difference appears to be in the observation that in butanone the majority of the tris(diaminoethane) complex remains unchanged, while in acetone NiN_4 species predominate after a short period. The acetone products $[Ni(6)_2]^{2+}$, $[Ni(8)]^{2+}$, and $[Ni(10)]^{2+}$, and their butanone analogues $[Ni(7)_2]^{2+}$, $[Ni(9)]^{2+}$, and $[Ni(1)]^{2+}$, are all readily hydrolysed in the presence of diaminoethane, reforming the tris(diaminoethane)nickel(II) cation. The difference in the reactions in the two ketones could therefore be explained if the equilibrium represented below was displaced to the right in acetone, to the left in butanone.

$$[Ni(en)_2]^{2+} + \text{ketone} \rightleftharpoons [Ni(en)_2]^{2+} + (\text{en–ketone}) + H_2O$$

where (en–ketone) represents imines, β-aminoketones, *etc.* The $[Ni(en)_2]^{2+}$ reacts further with acetone to form $[Ni(8)]^{2+}$ and other unidentified NiN_4 species, which react irreversibly to form $[Ni(4)]^{2+}$ and $[Ni(5)]^{2+}$. With butanone, $[Ni(7)_2]^{2+}$ is formed within the equilibrium, since it does not increase in amount with time. An irreversible reaction many orders of magnitude slower than with acetone yields $[Ni(3)]^{2+}$, but reactions which would yield $[Ni(2)]^{2+}$ are completely inhibited.

Support for this hypothesis is provided by the reaction of $[Ni(8)]^{2+}$, $[Ni(9)]^{2+}$, $[Ni(10)]^{2+}$, and $[Ni(1)]^{2+}$ with diaminoethane. In methanol these give mauve, triplet ground state adducts, *e.g.* $[Ni(8)en]^{2+}$, which hydrolyse readily to give $[Ni(en)_3]^{2+}$ if appreciable water is present. In acetone solution the mauve colour formed when diaminoethane is added to a yellow solution of *e.g.* $[Ni(8)]^{2+}$ reverts to yellow within seconds, as expected if the free diaminoethane concentration was being rapidly reduced, (and $[Ni(5)]^{2+}$ is ultimately formed).[2] In butanone the mauve colour of the adduct remains, and after a few days the solution is indistinguishable from a solution prepared by dissolving tris(diaminoethane)-nickel(II) perchlorate.

The large difference in the rate of the reaction of tris(diaminoethane)nickel(II) with acetone and butanone thus does not appear to arise from a large difference in the rate of reaction of these chemically similar ketones, either to form co-ordinated imines or β-aminoketones, but is associated with differences in equilibrium constants, in which the chemical differences between the ketones are magnified by their differences as solvents.

Copper(II)-*Diaminoethane–Butanone Reactions*.—When bis(diaminoethane)copper(II) perchlorate was reacted with butanone at room temperature, or under reflux, the colour changed from magenta to deep blue, but only starting material could be isolated crystalline from the solution. At higher temperatures, reaction occurs to give $[Cu(1)]^{2+}$ and ultimately $[Cu(2)]^{2+}$. Bis(diamino-

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

ethane)copper(II) reacts with acetone at room temperature to yield a pentadentate β-aminoketone complex.[2]

Diaminoethane–Butanone Reaction.—When diaminoethane was reacted with butanone at room temperature, or under reflux, the initially colourless solution slowly became yellow. Addition of nickel(II) perchlorate (Ni : en = 1 : 2) resulted in the formation of $[Ni(4)]^{2+}$. However, since bis(diaminoethane)nickel(II) reacts with butanone to yield $[Ni(4)]^{2+}$ this does not prove that the β-aminoketone is present in the solution. Similar addition of copper(II) perchlorate yielded only bis(diaminoethane)copper(II) perchlorate. The analogous set of reactions with acetone in place of butanone yielded a copper(II) pentadentate β-aminoketone complex, and ultimately $[Ni(4)]^{2+}$.[2]

Diaminoethane Monohydroperchlorate–Butanone Reaction.—The monohydroperchlorate of diaminoethane reacted rapidly with butanone to yield the crystalline dihydroperchlorate of the macrocycle (2), as for the similar reaction with acetone to yield $[H_2(5)](ClO_4)_2$.[2,8]

The compound $[H_2(2)](ClO_4)_2$ reacted with nickel(II) acetate to yield the same products as obtained by cyclization of $[Ni(4)](ClO_4)_2$ in pyridine. With copper(II) acetate, a product isomeric with that reported earlier,[5] formed by prolonged reaction of bis(diaminoethane)copper(II) with butanone was obtained.

Further compounds of (2) with nickel(II) and cobalt(III), formed from $[H_2(2)](ClO_4)_2$, will be described elsewhere.[8a]

Stereochemistry of the Macrocyclic Complexes.—The i.r. spectra of the pair of compounds $[M(2)](ClO_4)_2$, M = Ni^{II}, Cu^{II}, are very similar, including details of the 'fingerprint' region, and in view of the similarities in their modes of preparation it is reasonable to conclude that the cations represented as $[Ni(3)]^{2+}$ and $[Cu(3)]^{2+}$ have the same structure. The spectra of the $[M(3)](ClO_4)_2$ pair do not show any close similarity.

The isomerism of the cations $[M(2)]^{2+}$ and $[M(3)]^{2+}$ could be geometric (*i.e.* the 4,11- and 4,14-diene complexes, as represented in the formulae) or optical [*rac* and *meso* configurations arising from the pair of chiral carbon centres present for (2) or (3)] in origin. Macrocyclic complexes $[Ni(4)]^{2+}$, and the 1,2-diaminopropane analogue, formed *via* bis(β-aminoketone) complexes, or from the ligand salt obtained by reaction of the monoprotonated amine with acetone, have 4,11-diene structures.[2,3] The stereochemistry of (2) and (4) with nickel(II) and cobalt(III) are very similar, particularly in the relative stability of compounds in *abcd* (folded) and *bcde* (planar) co-ordination. Both are obtained in isomeric forms associated with the chiral co-ordinated secondary amine groups present. Both $[Ni(3)]^{2+}$ and $[Ni(5)]^{2+}$, the latter of known 4,14-diene structure,[9] have been obtained only in planar co-ordination, and in only one nitrogen configuration. Both $[Ni(2)]^{2+}$ and $[Ni(3)]^{2+}$ can be oxidized by nitric acid to form tetra-imine complexes (to be described elsewhere). These have properties very similar to the tetra-imine complexes formed by oxidation of $[Ni(4)]^{2+}$ and $[Ni(5)]^{2+}$ respectively.[10] In particular the compounds obtained from $[Ni(3)]^{2+}$ and $[Ni(5)]^{2+}$ are much darker in colour, and have a strong absorption band in the visible region of the electronic spectrum which can be assigned to the conjugated di-imine chromophore present for the 4,7,11,14-tetraene obtained from the 4,14-diene. It is reasonable to conclude that (2) and (3) have the 4,11- and 4,14-diene structures, respectively. This assignment is supported by the ^1H n.m.r. of the cations (to be published[8a]), which further indicates that both are present in the *C-meso* configurations. Related stereospecific condensations to yield macrocycles in *C-meso* configurations occur with 1,2-diaminopropane and acetone[3] and with diaminoethane and benzilidene acetone.[10]

Spectroscopic Properties.—The i.r. and *d–d* spectra (Experimental section) of the compounds are similar to those of previously reported analogues, and support the assigned structures.

EXPERIMENTAL

Caution. Perchlorates, particularly $[Ni(en)_2](ClO_4)_2$ and $[H(en)](ClO_4$, should be treated with due care. Shock sensitivity has not been observed, but the compounds may explode if heated above *ca.* 200°.

Bis(8-amino-5-ethyl-5-methyl-6-azaoctan-3-one)nickel(II) *Perchlorate*, $[Ni(9)_2](ClO_4)_2$.—A solution of bis(diaminoethane)nickel(II) perchlorate in butanone was left for one week. The blue crystalline product was filtered off and recrystallized from hot methanol, or hot methyl cyanide–ethanol (Found: C, 37·7; H, 7·0; Ni, 9·5. $C_{20}H_{44}Cl_2N_4NiO_{10}$ requires C, 38·1; H, 7·0; Ni, 9·3%).

(13-*Amino*-8,10-*diethyl*-3,8-*dimethyl*-4,7,11-*triazatrideca*-3,-10-*diene*)*nickel*(II) *Perchlorate*, $[Ni(10)](ClO_4)_2$.—The previous reaction was carried out in methanol–butanone (1 : 1), reacting for one week at room temperature for 8 h under reflux, and then allowing the methanol to evaporate. The yellow crystalline *product* was recrystallized from hot methyl cyanide–ethanol (Found: C, 35·3; H, 6·2; N, 10·4; Ni, 11·1. $C_{16}H_{34}Cl_2N_4NiO_8$ requires C, 35·6; H, 6·3; N, 10·4; Ni, 10·9%).

(4,6-*Diethyl*-6-*methyl*-3,7-*diazanon*-3-*ene*-1,9-*diamine*)-*nickel*(II) *Tetrachlorozincate*, $[Ni(1)]ZnCl_4$.—Di-μ-chloro-bis-{bis(diaminoethane)nickel(II)}chloride, $[Ni_2(en)_4Cl_2]Cl_2$, was reacted with methanol–butanone (1 : 1) until it dissolved completely to form a brown solution (*ca.* one week for 20 g in 250 ml at room temperature, or one day under reflux). An excess of zinc chloride dissolved in ethanol was added, when the orange product crystallized. This was recrystallized from hot water–methanol (Found: C, 29·5; H, 5·9; N, 11·4; Ni, 11·9. $C_{12}H_{28}Cl_4N_4NiZn$ requires C, 29·2; H, 5·7; N, 11·4; Ni, 11·8%).

(5,7,12,14-*Tetraethyl*-7,14-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*) *Dihydroperchlorate*, $[H_2(2)](ClO_4)_2$.—Diaminoethane monohydroperchlorate, prepared by rotary evaporation of an aqueous solution containing equimolar

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[8] N. F. Curtis and R. W. Hay, *Chem. Comm.*, 1966, 524.

[8a] N. F. Curtis, *Austral. J. Chem.*, in the press.

[9] B. T. Kilbourn, R. Ryan, and J. D. Dunitz, *J. Chem. Soc.* (*A*), 1969, 2407.

[10] N. F. Curtis, *J. Chem. Soc.* (*A*), 1971, 2834; V. L. Goedken and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 2679.

amounts of diaminoethane and perchloric acid, was dissolved in butanone (10 g in 100 ml). After 24 h the white crystalline product was filtered off and washed with ethanol. A sample for analysis was recrystallized from hot methanol (Found: C, 44·8; H, 7·7; N, 10·1. $C_{20}H_{42}Cl_2N_4O_8$ requires C, 44·8; H, 7·9; N, 10·0%).

(5,7,12,14-*Tetraethyl*-7,14-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*nickel*(II) *Perchlorate*, [Ni(2)](ClO_4)$_2$.—The dihydroperchlorate of the ligand (previous preparation) was warmed in methanol with a small excess of nickel(II) acetate until it all dissolved. The solution was allowed to evaporate, when the orange *product* crystallized. The compound is very sparingly soluble in water, from which it tends to separate as an oil. Recrystallization is conveniently effected by adding water to a solution in methyl cyanide or acetone (it is very soluble in these solvents if 5% of water is present) until turbid, and allowing the solution to evaporate slowly. The product obtained is in the β (N-*meso*) configuration (Found: C, 40·6: H, 6·8; N, 9·2; Ni, 10·0. $C_{20}H_{40}Cl_2N_4NiO_8$ requires C, 40·5; H, 6·8; N, 9·5; Ni, 9·9%).

(5,7,12,14-*Tetraethyl*-7,14-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,11-*diene*)*copper*(II) *Perchlorate*, [Cu(2)](ClO_4)$_2$.—As for the previous preparation, using copper(II) acetate (Found: C, 40·2; H, 6·7; N, 9·5. $C_{20}H_{40}Cl_2CuN_4O_8$ requires C, 40·0; H, 6·8; N, 9·4%).

(5,7,12,14-*tetraethyl*-7,12-*dimethyl*-1,4,8,11-*tetra-azacyclotetradeca*-4,14-*diene*)*nickel*(II) *Perchlorate*, [Ni(3)](ClO_4)$_2$.—This preparation is reported by Blight.[6] Tris(diaminoethane)nickel(II) perchlorate hemihydrate was heated in a sealed tube at 120° with butanone–methanol (1 : 1) for a period of weeks. The cold liquid was decanted, and the residue boiled with methanol, cooled, and filtered. The combined liquids were treated with charcoal, rendered acidic with perchloric acid and allowed to evaporate. Further product was obtained by boiling the charcoal with several successive portions of water, followed by slow evaporation of the combined filtrates. The yellow crystalline *product* was recrystallized from hot water. Yield 0—5% dependent on time of heating (Found: C, 40·2; H, 6·8; N, 9·4. $C_{20}H_{40}Cl_2N_4NiO_8$ requires C, 40·5; H, 6·8; N, 9·5%).

Spectroscopic Data.—I.r. functional group frequencies (cm^{-1}) and *d–d* electronic spectra (nm, molecular extinction coefficient in parentheses): [Ni(1)]$ZnCl_4$: ν(NH_2), 3245, 3190; ν(NH), 3100; * ν(C:N), 1645; δ(NH_2), 1590, 1560sh; water, 482 (65). [H_2(2)](ClO_4)$_2$: ν(NH), 3180; ν(C:N), 1650; δ(NH_2^+), 1530. N-*meso*-[Ni(2)](ClO_4)$_2$: ν(NH), 3180; ν(C:N), 1648; methanol–$HClO_4$,† 450 (62). N-*meso*-[Cu(2)](ClO_4)$_2$: ν(NH), 3120; ν(C:N), 1657; methanol/$HClO_4$,† 510 (110). [Ni(3)](ClO_4)$_2$: ν(NH), 3205, 3180; ν(C:N), 1658; methanol/$HClO_4$,† 432 (148). [Ni(7)$_2$](ClO_4)$_2$: ν(NH_2), 3339, 3291, 3240, 3190; ν(C:O), 1673; δ(NH_2), 1597; reflectance, (ν_1), 955; ‡ (ν_2),§ 545; [Ni(9)](ClO_4)$_2$: ν(NH_2), 3275, 3245; ν(NH), 3195, 3170; ν(C:N), 1660; δ(NH_2), 1600; water, 455 (107).

[3/1538 *Received*, 23*rd July*, 1973]

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* The (NH_2)/(NH) bands of the tetrachlorozincate is broadened, and displaced to lower frequency compared with the perchlorate salt, indicating hydrogen bonding between the amino group and tetrachlorozincate anion.

† 80% Methanol, 20% of 1M $HClO_4$, to prevent inversion at the nitrogen centres.

‡ $^3T_{1g} \leftarrow {}^3A_{2g}$ in O_h. This band shows no indication of the splitting characteristic of the *trans*-NiN_4O_2 chromophore.

§ $^3T_{2g}(F) \leftarrow {}^3A_{2g}$ in O_h.