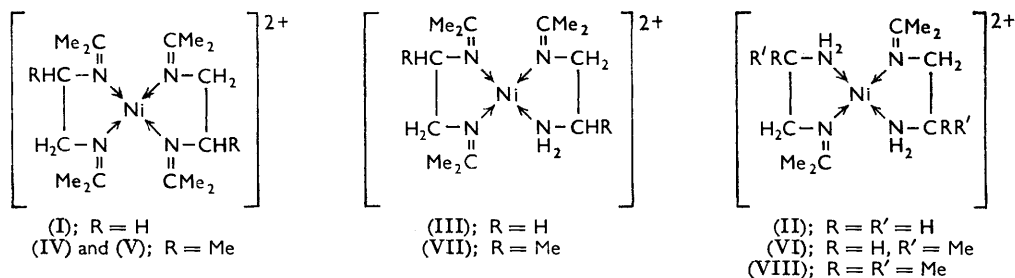**231.** *Transition-metal Complexes with Aliphatic Schiff Bases. Part II.*[1] *Nickel*(II) *Complexes with* N-*Isopropylidene-substituted Schiff Bases derived from Some* C-*Substituted Ethylenediamines.*

By MARGARET M. BLIGHT and N. F. CURTIS.

Reactions of the nickel complexes of some *C*-substituted ethylene-diamines with acetone to form square-planar, diamagnetic, *N*-isopropylidene Schiff-base co-ordination compounds are described. With propylene-diamine, di-, tri-, and tetra-*N*-isopropylidenebisdiamine compounds were formed, the latter existing in two non-interconvertible forms. With 2-methylpropylenediamine, only a di-*N*-isopropylidene compound was formed, whilst there was no reaction with 2,3-diaminobutane, or with *meso*-stilbenediamine. The visible and ultraviolet absorption spectra of these compounds are described.

THE reaction of nickel ethylenediamine co-ordination compounds with acetone to form yellow, diamagnetic complexes with *N*-isopropylidene-ethylenediamine Schiff bases was described in Part I.[1] Trisethylenediaminenickel perchlorate reacts with acetone at room temperature to form bis-(*NN'*-di-isopropylidene-ethylenediamine)nickel perchlorate (I), and bisethylenediaminenickel perchlorate reacts with hot acetone to form the compounds with two (II) and three (III) *N*-isopropylidene groups, and on prolonged ultraviolet irradiation to form the tetra-*N*-isopropylidene compound (I). The last compound shows exceptional resistance to hydrolysis, being unaffected by concentrated acids or alkalis; the di-*N*-isopropylidene compound (II) is hydrolysed by dilute mineral acids. The tri-*N*-isopropylidene compound (III) is the least stable, being readily hydrolysed by dilute acetic acid, and in aqueous solution slowly changed into the di-*N*-isopropylidene derivative. The resistance towards hydrolysis of all these compounds is unusual, Schiff-base complexes usually being rapidly hydrolysed by water.[1]

(I); R = H
(IV) and (V); R = Me

(III); R = H
(VII); R = Me

(II); R = R' = H
(VI); R = H, R' = Me
(VIII); R = R' = Me

The anion is ClO_4^-

Note. These formulae indicate general structure, not absolute configuration.

Preparation.—Trispropylenediaminenickel perchlorate reacts with acetone much less readily than does the trisethylenediamine. The reaction is catalysed by bases, such as propylenediamine or pyridine. From the reaction mixture approximately equal amounts of orange and of yellow crystals can be isolated, this colour difference persisting in solution, and in salts with a variety of anions. The two forms, which can be separated by fractional crystallisation, are isomers of bis-(*NN'*-isopropylidenepropylenediamine)nickel(II) per-chlorate (IV, yellow form; V, orange form). Both forms have chemical and physical properties similar to those of the ethylenediamine analogue (I), being similarly resistant to acid hydrolysis. Like the tetraisopropylidene-compound (I), they are decomposed by powerful oxidising agents (*e.g.*, by acid permanganate or boiling peroxydisulphate) and by cyanide ions, in both cases, the orange form (V) more readily than the yellow (IV). They

[1] Part I, Curtis, *J.*, 1960, 4409.

are also decomposed slowly by sodium hydroxide solution at 130°, form (IV) more rapidly than (V). Heating acid, alkaline, or neutral solutions at 130° caused no interconversion of the two forms.

The two forms give different X-ray powder-diffraction patterns, and have different electronic absorption spectra, described below. The infrared spectra are very similar and both are similar to that of (I), with minor changes caused by the introduction of the methyl groups. These spectra all have strong absorption at 1660 cm.$^{-1}$, caused by the C:N groups. The infrared spectra and the nature of the isomerism will be discussed more fully later.

No product could be isolated after long irradiation of anhydrous bispropylenediamine-nickel perchlorate in acetone with ultraviolet light. From the bisethylenediamine compound, the tetra-N-isopropylidene compound (I) was produced under these conditions.

Bispropylenediaminenickel perchlorate reacts with acetone at 100—110°, the initial product being yellow NN'N''-tri-isopropylidenebispropylenediaminenickel(II) perchlorate (VI). If the reaction is continued, the NN'-di-isopropylidenebispropylenediamine-nickel(II) compound (VII) becomes the major product. This was isolated as the orange tetrachlorozincate, the perchlorate being extremely soluble. These compounds have properties similar to their ethylenediamine analogues, but are less easily hydrolysed. In aqueous solution the tri-N-isopropylidene compound is slowly hydrolysed to the di-N-isopropylidene compound, $t_{\frac{1}{2}}$ being many days at room temperature, about 15 minutes at 100°.

Bis- and tris-(2-methylpropylenediamine)nickel perchlorate both react with acetone more rapidly than do their ethylenediamine analogues, in both cases yielding NN'-di-isopropylidenebis-(2-methylpropylenediamine)nickel(II) perchlorate monohydrate (as VIII). All attempts to prepare compounds with more than two Schiff-base groups, by prolonged heating or ultraviolet irradiation of acetone solutions, were unsuccessful. This compound has properties similar to the ethylenediamine (III) and propylenediamine (VII) analogues, the resistance to acid hydrolysis being intermediate between those of (III) and (VII), although the solubility in water is much less.

When bis- or tris-2,3-diaminobutanenickel perchlorate in acetone solution was heated at 110°, or irradiated with ultraviolet light, the solutions slowly became brown, but only unchanged material could be isolated. (Brown, tarry acetone polymers are also formed during the reactions of the other diamine complexes.) Similar attempts to prepare Schiff-base complexes from nickel *meso*-stilbenediamine complexes were likewise unsuccessful.

Magnetic Susceptibilities.—All the compounds are diamagnetic. Susceptibilities were measured for the solid by Gouy's method.

Visible and Ultraviolet Absorption Spectra.—The visible spectra of these compounds are similar, although the amount of π bonding by the nickel must vary. The peak is shifted from its position in the singlet form of the simple bisdiamine, 450 mμ for ethylene-diamine and propylenediamine,[2] and 445 mμ for 2-methylpropylenediamine.[3]

The peak at 260—280 mμ is possibly associated with a transition involving the π electrons of the azomethine groups, conjugated by π bonding by using the nickel d_{xz} and d_{yz} orbitals. Thus, the extinction coefficient increases from about 2000 to 5000 as the number of azomethine groups increases from 2 to 4. This assignment is supported by the fact that the spectra of copper(II), palladium(II), and platinum(II) analogues, to be described subsequently, show similar bands, although the extinction coefficient for copper(II) compounds with two and with four C:N groups are approximately the same; also, this peak is absent from the spectra of the saturated compounds produced by hydrogenation (to be described later), although the rest of the spectrum is similar. The 205—220 mμ peak, for which the extinction coefficient is unrelated to the number of C:N groups, probably arises from a charge-transfer transition.

[2] Sone and Kato, *Z. anorg. Chem.*, 1959, **301**, 277.
[3] Curtis, Thesis, University of New Zealand, 1954.

Discussion.—The physical and chemical properties of these compounds indicate that they have structures analogous to those of the ethylenediamine compounds.[1]

Visible absorption spectra in aqueous solution.

	Diamine	C:N groups	$\lambda_{max.}$ (mμ)	ε	$\lambda_{\frac{1}{2}}$ (mμ)
(I)	en	4	436	104	400—472
(IV)	pn	4	422	95	387—453
(V)	pn	4	437	78	398—481
(III) *a*	en	3	434	105	397—472
(VI)	pn	3	429	104	392—467
(II)	en	2	435	70	399—471
(VII)	pn	2	430	78	392—465
(VIII)	2-Me.pn	2	426	83	390—460

a The spectrum reported for this compound in Part I is incorrect, the rate of transition to (II) being much greater than was realised.

Ultraviolet absorption spectra in aqueous solution.

	Diamine	C:N groups	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
(I)	en	4	280	5400	238	8000 *c*	213	17,000
(IV)	pn	4	279	5500	239	7000 *c*	210	17,000
(V)	pn	4	283	4900	244	8000 *c*	220	15,000
(III)	en	3	270	2400	—		209	20,000
(VI)	pn	3	266	2900	—		212	20,000
(II)	en	2	265	2100	—		205	15,000
(VII) *b* ...	pn	2	262	2100	—		207	21,000
(VIII)	2-Me.pn	2	262	2000	—		208	17,000

b The solution of the tetrachlorozincate was passed through an ion-exchange column in the perchlorate form before measurement of the spectrum. *c* This peak is present as a shoulder on the adjacent more intense peak. The compound peak was separated into " gaussian " curves, but the position and intensity of the minor band is somewhat dependent on the half-width of the major band (assumed to be similar to that in the spectra of the di- and tri-*N*-isopropylidene compounds.

Ethylenediamine and propylenediamine nickel complexes react with acetone to form Schiff-base complexes with two, three, and four *N*-isopropylidene groups. With 2-methylpropylenediamine, only a di-*N*-isopropylidene derivative is formed, while the 2,3-diaminobutane and stilbenediamine complexes do not react. The formation of a tetra-*N*-isopropylidene compound with propylenediamine shows that a methyl group α to the amino-group does not prevent formation of a Schiff base in this position. Some indication of the relative stabilities is obtained from the rate of acid hydrolysis, which is greater for the di- and tri-*N*-isopropylidene compounds formed from ethylenediamine, than for those from propylenediamine and 2-methylpropylenediamine. Thus, in a phthalate buffer at pH = 4, the tri-*N*-isopropylidene compound (III) from ethylenediamine is hydrolysed in a few minutes at room temperature, while that (VI) from propylenediamine is hydrolysed only during several hours. Similarly, in aqueous solution, (III) is hydrolysed to the di-*N*-isopropylidene compound (II) more rapidly than the di-*N*-isopropylidene compound (VI) is to (VII).

It thus appears that lack of reaction between 2,3-diaminobutane and acetone is not due to instability of the product but is of kinetic origin. Investigation of the trisethylenediaminenickel–acetone reaction shows the first step to be kinetically of first order in both complex and ketone, catalysed by bases, and retarded by water, suggesting that this step is the formation of the first azomethine group. In 2,3-diaminobutane and stilbenediamine both the amino-groups are adjacent to a methyl or phenyl group, whereas with the other diamines, at least one of the amino-groups is not so placed, suggesting that steric hindrance of this first step is the determining factor. Work on the mechanism of these reactions is proceeding.

[*Added in proof.* Recent evidence suggests that these compounds may have an isomeric structure.[7]]

EXPERIMENTAL

2-Methylpropylenediamine was prepared by the catalytic hydrogenation of α-acetamidoiso-butyronitrile in acetic anhydride.[4] The resultant diacetyl derivative was hydrolysed by alkali, this giving an improved yield of diamine. 2,3-Diaminobutane was prepared by the reduction of dimethylglyoxime, nickel–aluminium alloy being used in alkaline solution.[5] *meso*-Stilbenediamine was prepared by Mills and Quibbell's method.[6]

Bis-(NN'-di-isopropylidenepropylenediamine)nickel(II) *Perchlorate* (IV and V).—An acetone solution of trispropylenediaminenickel(II) perchlorate was irradiated with ultraviolet light for several days, the blue-violet colour changing to brown. The less-soluble orange form often crystallised during the irradiation. The solution, filtered from any orange crystals, was evaporated to dryness, and the residue heated to 100° in a vacuum to remove any volatile acetone polymers. The residue was dissolved in hot water (charcoal), and the solution filtered whilst hot and allowed to cool; the two forms crystallised together. These were separated by fractional crystallisation from aqueous solution, the yellow form being the more soluble at room temperature. The separated compounds (total yield, after extraction of the charcoal, with boiling water, ~70%) were recrystallised from hot water [Found, for yellow form: Ni, 10·2; C, 38·7; H, 6·4; N, 9·6. Found, for orange form: Ni, 10·2; C, 38·6; H, 6·4; N, 9·6. $C_{18}H_{36}N_4Ni(ClO_4)_2$ requires Ni, 10·4; C, 38·2; H, 6·4; N, 9·9%].

NN'N''-Tri-isopropylidenebispropylenediaminenickel(II) *Perchlorate* (VI).—Anhydrous bis-propylenediaminenickel perchlorate (formed by vacuum desiccation of the dihydrate) was heated with acetone and anhydrous calcium sulphate in a sealed tube at 110° for 1 hr. The filtered solution was evaporated to dryness and the residue dissolved in a little hot methanol, the *perchlorate* separating as yellow crystals (yield 10%) [Found: Ni, 11·1; C, 34·0; H, 6·4; N, 10·7. $C_{15}H_{32}N_4Ni(ClO_4)_2$ requires Ni, 11·2; C, 34·3; H, 6·1; N, 10·7%].

NN'-Di-isopropylidenebispropylenediaminenickel(II) *Tetrachlorozincate* (VII).—The reaction mixture described in the previous preparation was heated at 110° for 2 hr., the filtered solution evaporated to dryness, the residue dissolved in water, and the solution boiled for 30 min. to ensure complete conversion into the di-*N*-isopropylidene compound. The solution (charcoal) was filtered hot, the filtrate evaporated to dryness, the residue dissolved in methanol, and a concentrated solution of sodium tetrachlorozincate added, followed by acetone to complete precipitation. The *salt* was recrystallised from hot methanol as pale orange crystals (yield 60%) (Found: Ni, 11·9; C, 29·3; H, 5·7; N, 12·8; Cl, 28·9. $C_{12}H_{28}N_4Cl_4NiZn$ requires Ni, 11·9; C, 29·2; H, 5·7; N, 13·0; Cl, 28·8%].

NN'-Di-isopropylidenebis-(2-methylpropylenediamine)nickel(II) *Perchlorate Monohydrate* (VIII).—A solution of tris-(2-methylpropylenediamine)nickel perchlorate in acetone was boiled for 15 min., or a solution of bis-(2-methylpropylenediamine)nickel perchlorate in acetone was heated at 100° for 30 min. and the *product* (yield, 80%) obtained as in the above experiments [Found: Ni, 11·2; C, 31·7; H, 6·3; N, 10·4. $C_{14}H_{30}N_4ONi(ClO_4)_2$ requires Ni, 11·1; C, 31·6; H, 6·4; N, 10·6%].

Note.—NN'N''-Tri-isopropylidenebisethylenediaminenickel perchlorate (III), for which a preparation was described in Part I, can be more conveniently prepared by heating dipyridine-bisethylenediaminenickel perchlorate (which is precipitated when pyridine is added to a solution of the dihydrate in alcohol) for 1½ hr. at 100° with 1 : 1 methanol–acetone with an excess of anhydrous calcium sulphate. The filtered solution was evaporated to dryness under vacuum, and the residue dissolved in a little hot methanol; the product (yield, 60%) separated on cooling.

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