855. *Transition-metal Complexes with Aliphatic Schiff Bases. Part I. Nickel*(II) *Complexes with* N-*Isopropylidene-ethylenediamine Schiff Bases.*

By N. F. CURTIS.

Nickel(II) diamine complexes react with aliphatic ketones to form nickel(II) Schiff base co-ordination compounds. Although the parent imines are too unstable to be isolated, the complexes are extremely stable. Possible structures are discussed in terms of the unusual chemical inertness.

HITHERTO, co-ordination compounds of α-di-imines have usually been prepared by reaction between the pre-formed di-imine and the appropriate metal salt under anhydrous conditions. As aliphatic imines are usually too unstable to be isolated, most of the compounds reported have been formed from aromatic di-imines. Bahr[1] describes the compounds (I; R = Me or Ph, R′ = Ph or C_6H_4Me, M = Ni^{2+}, Cu^{2+}, or Zn^{2+}), all of which are readily decomposed by water. Hoyer[2] describes the formation of the cupric complex

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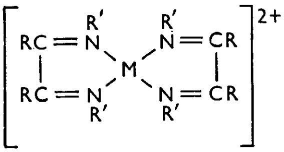
[1] Bahr, *Z. anorg. Chem.*, 1951, **267**, 137; Bahr and Kretzer, *ibid.*, p. 161.

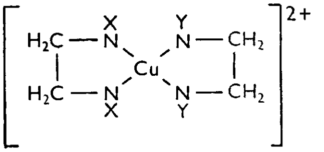
[2] Hoyer, *Naturwiss.*, 1959, **46**, 14.

of *NN'*-difurfurylidene-ethylenediamine (II) which is rapidly hydrolysed by alcohol containing the correct quantity of water to the compound (III), which is itself readily hydrolysed to the simple ethylenediamine complex.

Krumholz [3] reports the formation of ferrous derivatives of biacetyl (and glyoxal) bis-*N*-methylimine (IV) by reaction of ferrous salts, biacetyl (or glyoxal), and excess of methylamine. These compounds are stable in aqueous solution, and decompose in acid or alkaline solution only on boiling. Methylamine and biacetyl can be recovered from the hydrolysis products. However, the infrared absorption spectrum of tris(biacetylbismethylimine)-iron(II) iodide shows no absorption in the region characteristic of C:N groups, and hence the imine structure must be regarded as doubtful.[4]

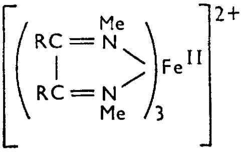


(I)



(II); X=Y= furfurylidene

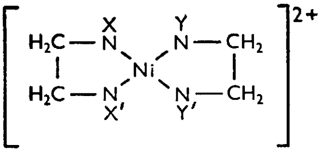
(III); X=H_2, Y= furfurylidene



(IV)

Preparation.[5]—When trisethylenediaminenickel(II) perchlorate is dissolved in anhydrous acetone, the colour of the solution slowly changes from blue-violet to yellow. From the resultant solution bis-(*NN'*-di-isopropylidene-ethylenediamine)nickel(II) perchlorate (V) can be isolated. The reaction can be speeded by the addition of bases, such as pyridine or ethylenediamine, by heating, or by exposure to ultraviolet light. The presence of traces of water retards the reaction. The same product is formed, but much more slowly, if a solution of anhydrous bisethylenediaminenickel(II) perchlorate in acetone is exposed to ultraviolet light. When this perchlorate reacts with acetone, in the absence of ultraviolet light, two products can be isolated, depending on the conditions. The initial product is (*NN'N''*-tri-isopropylidenebisethylenediaminenickel(II) perchlorate (VI). If the reaction is continued, the *NN'*-bisisopropylidene compound, (VII) or (VIII), becomes the major product.

The perchlorates (V) and (VI) form bright yellow crystals, sparingly soluble in cold water, alcohols, acetone, etc.; (VII) [or (VIII)] forms large orange crystals, and is much more soluble than the other two. All three are diamagnetic as the solid and in aqueous solution; (V) is chemically very stable, being unattacked by boiling concentrated acids or alkalis, and being decomposed only by powerful oxidising agents, such as chloric acid, or peroxydisulphate, and by cyanide ions; the other two perchlorates, particularly (VI), are less resistant, being decomposed by dilute acids, and by any reagent which removes nickel ions from solution, such as hydrogen sulphide or ammoniacal dimethylglyoxime Perchlorates (VI) and (VII) are relatively stable in boiling aqueous solution, but on prolonged boiling (~20 hr.) with aqueous pyridine, the former is converted into the latter.



(V); X = X' = Y = Y' = CMe_2

(VI); X = H_2, X' = Y = Y' = CMe_2

(VII); X = Y' = H_2, X' = Y = CMe_2

(VIII); X = X' = H_2, Y = Y' = CMe_2

Visible and Ultraviolet Absorption Spectra.—The visible spectra of these compounds are very similar, there being one peak at 436 mμ. The ultraviolet absorption spectra of (VI)

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[3] Krumholz, *J. Amer. Chem. Soc.*, 1953, **75**, 2163.
[4] Busch and Bailar, *J. Amer. Chem. Soc.*, 1956, **78**, 1137
[5] Curtis, Thesis, University of New Zealand, 1954

and (VII) are the same, showing two peaks which are ascribed to the imine groups conjugated through π-bonding by the nickel atom. This conjugation would be expected to be more efficient in the case of (V), which has four symmetrically arranged isopropylidene groups, and in (V) the two peaks in the ultraviolet spectra of the previous compounds are displaced to longer wavelengths, and an additional peak appears as a shoulder.

Absorption spectra in aqueous solution.

	$\lambda_{max.}$ (mμ)	ε		$\lambda_{max.}$ (mμ)	ε
(V)	436	104	(VI) and (VII)	436	70
	282	5,400		268	2,100
	238	7,900		—	—
	213	17,300		205	15,000

Infrared Spectra.—The infrared spectra support the suggested Schiff-base structures for these compounds. Thus all three show absorption in the C:N stretching region, the relative intensity increasing in the order (VII) < (VI) < (V), as the number of C:N groups in the molecule increases; (VI) and (VII) show absorption in the NH_2 stretching and deformation regions. In (VI), with one NH_2 and three C:N groups, the height of the NH_2 deformation peak is less than that of the C:N stretching peak, with the relative heights reversed in (VII), with two NH_2 and two C:N groups. Work on the infrared spectra of these, and related compounds, is proceeding.

Discussion.—Diamagnetic four-co-ordinate nickel(II) complexes are normally square planar.[6] The azomethine group C:N is also planar in structure. The molecule of (V) is required by these conditions to be coplanar, but a planar model, with standard covalent radii, indicates that there would be considerable interference between the methyl groups of adjacent isopropylidene groups, which must be removed by the skewing of the molecule. The strain resulting from such distortions would be expected to decrease the stability of the molecule. This effect is probably responsible for the fact that (VI), with three isopropylidene groups, is less stable than (VII), which has only two, and consequently no strain. However, the bis-(*NN'*-difurfurylidene-ethylenediamine)copper(II) ion, which is "strain free," is very readily hydrolysed,[2] but the cupric analogue of (V) (to be described in a subsequent paper) shows stability comparable with that of the nickel compound.

Schiff bases are usually readily hydrolysed, by water or by dilute acids, and hence the resistance of these compounds is unusual, especially as the parent Schiff base, *NN'*-di-isopropylidene-ethylenediamine cannot be isolated, whereas the compounds reported by Bahr[1] and Hoyer,[2] for which the parent Schiff bases are first prepared, are all hydrolysed very readily. It has been reported that ease of hydrolysis of Schiff bases is affected by co-ordination,[7] and it has been suggested that an ethylenedi-imine complex, which on hydrolysis can form the stable ethylenediamine complex, will be more easily hydrolysed than a biacetyl di-imine, for which the co-ordinating power is greatly reduced on hydrolysis. On this basis, the isopropylidene-ethylenediamine complex would be expected to be readily hydrolysed, like Hoyer's furfurylidene-ethylenediamine complexes.[2]

The strain inherent in structure (V) would be removed by the tautomeric change to structure (IX), in which the interference between the methyl groups is eliminated, and the C:N groups are conjugated and endocyclic. Bahr[1] was able to prepare complexes only with di-imines which gave this configuration. However, it has been reported that $R\cdot CH{:}N\cdot CH_2R'$ will not rearrange to $R\cdot CH_2\cdot N{:}CHR'$, even when a quinonoid structure would result.[8] The tautomeric rearrangement produces complexes derived from biacetyl, similar to the ferrous compounds described by Krumholz,[3] which yielded biacetyl and the

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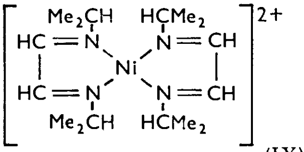
[6] Nyholm, *Chem. Rev.*, 1953, **53**, 263.

[7] Eichorn and Bailar, *J. Amer. Chem. Soc.*, 1953, **75**, 2905· Eichorn and Marchand, *ibid.*, 1956, **78**, 2688.

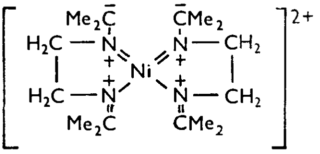
[8] Vaga, *Magyar Kem. Folyoirat*, 1939, **48**, 83.

parent amine on hydrolysis, but acetone was recovered from the solution, as the 2,4-dinitrophenylhydrazone, when (VI) was hydrolysed by dilute acid.

The rearrangement would not be required in the case of (VII) which is " strain free," but the absorption spectrum of this compound is closely similar to that of (VI), indicating closely related structures. From these considerations it appears that the rearrangement is unlikely.



(IX)



(X)

In (V), π-bonding by the nickel atom, using the suitably orientated d_ϵ-orbitals, amounting to resonance with forms such as (X) would be expected to occur. This, while increasing the co-ordinate bond strength, also reduces the strain of twisting the C:N groups by reducing their double-bond character. This would also reduce the tendency of the C:N groups to hydrolyse. The resonance would be less effective in the cases of the less symmetrical (VI) and (VII), accounting for their lower stability and resistance to hydrolysis. However, the remarkable difference in stability between the (*NN*-di-isopropylidenebisethylenediamine)nickel(II) ion (or its cupric analogue) and the (*NN'*-difurfurylidene-ethylenediamine)copper(II) ion remains unexplained.

EXPERIMENTAL

Bis-(NN'*-di-isopropylidene-ethylenediamine*)*nickel*(II) *Perchlorate.*—Trisethylenediaminenickel(II) perchlorate was dissolved in dry acetone, the solution stored for about 1 week and then evaporated to dryness, and the residue dissolved in a small quantity of hot water. This solution was boiled (charcoal) and filtered while hot. The yellow crystals which deposited on cooling were recrystallised from hot water; yield >80% [Found: Ni, 11·0; C, 35·7; H, 6·0; N, 10·0; ClO_4, 37·0. $C_{16}H_{32}N_4Ni(ClO_4)_2$ requires Ni, 11·4; C, 35·3; H, 5·8; N, 10·0; ClO_4, 37·0%].

(NN'N''*-Tri-isopropylidenebisethylenediamine*)*nickel*(II) *Perchlorate* (VI).—Powdered, blue bisethylenediaminenickel perchlorate dihydrate was placed in a vacuum desiccator fo rseveral days, the orange anhydrous salt being formed. This was dissolved in dry refluxing acetone. The condenser was then removed, and the solution immersed in a boiling-water bath; most of the acetone evaporated off, leaving a tarry residue. This was heated at 100° for 1 hr., the remaining acetone removed under vacuum, and the residue treated as in the previous preparation, yellow crystals being obtained; yields low and variable, usually 10—20% [Found: Ni, 11·8; C, 31·3; H, 5·6; N, 11·2. $C_{13}H_{28}N_4Ni(ClO_4)_2$ requires Ni, 11·6; C, 31·3; H, 6·0; N, 11·4%].

(*Di-*N*-isopropylidenebisethylenediamine*)*nickel*(II) *Perchlorate* [(VII) *or* (VIII)].—The tarry residue described in the previous preparation was heated at 100° for 6 hr., or at 120° for 2 hr. The product was treated as previously described. On slow evaporation of the final solution large orange crystals were formed. These were crystallised from water, by slow evaporation, or from hot methanol; yields variable, usually about 40% [Found: Ni, 12·8; C, 26·2; H, 5·2; N, 11·2; ClO_4, 43·4. $C_{10}H_{24}N_4Ni(ClO_4)_2$ requires Ni, 12·8; C, 26·5; H, 5·4; N, 11·2; ClO_4, 42·6%].

Spectra.—The infrared spectra were determined in potassium bromide discs, and in " Fluorolube " mulls, a Perkin-Elmer model 21 infrared spectrophotometer being used. The visible and ultraviolet spectra were determined in aqueous solution by using a Unicam model S.P. 500 spectrophotometer.

Analysis.—Nickel was determined as its dimethylglyoxime derivative. The perchlorate (V) was decomposed by boiling with an acid peroxydisulphate solution. Nitrogen was determined by the **Kjeldahl** method.

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