

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, VICTORIA UNIVERSITY OF WELLINGTON, WELLINGTON, NEW ZEALAND]

## Transition Metal Complexes with Aliphatic Schiff Bases. V. Copper(II) and Nickel(II) Complexes of 1,3-Propanediamine and Their Reactions with Acetone

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RECEIVED JULY 23, 1963

The preparation of  $\text{Ni}(\text{tmd})_3(\text{ClO}_4)_2$  (I),  $\text{Ni}(\text{tmd})_2(\text{py})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (II),  $\text{Ni}(\text{tmd})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (III),  $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_3$  (IV), and  $\text{Cu}(\text{tmd})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  (V) (tmd = 1,3-propanediamine, py = pyridine) is described. Reaction of the perchlorate salts with acetone gives initially Schiff base complexes containing two coordinated N-isopropylidene groups. Further reaction of acetone with I or IV gives complexes containing a cyclic quadridentate ligand coordinated by two secondary amine and two azomethine donor groups. The absorption spectra and diamagnetism of the nickel(II) Schiff base complexes indicate square-planar structures.

Previous papers in this series<sup>1-4</sup> have described the compounds prepared by condensing aliphatic ketones with 1,2-diamines<sup>1-3,5</sup> and triethylenetetramine<sup>4</sup> complexes of copper(II) and nickel(II). This paper describes the compounds formed by the reaction of acetone with 1,3-propanediamine (trimethylenediamine = tmd) copper(II) and nickel(II) perchlorates.

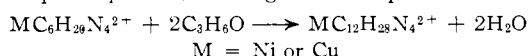
There has been relatively little recent work on the synthesis of copper(II) and nickel(II) complexes using 1,3-propanediamine as a ligand. The nickel(II) complexes  $\text{Ni}(\text{tmd})_3\text{PtCl}_4$ ,  $\text{Ni}(\text{tmd})_2(\text{SCN})_2$ ,  $\text{Ni}(\text{tmd})_2\text{SO}_4$ , and  $\text{Ni}(\text{tmd})_2(\text{C}_4\text{H}_8\text{O}_2\text{N})_2$  have been prepared by Tschugaeff<sup>6,7</sup> and the copper(II) complexes  $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_2$  and  $\text{Cu}(\text{tmd})_2(\text{O}-\text{SO}_2-\text{C}_{10}\text{H}_7)_2$  by Pfeiffer and his co-workers.<sup>8</sup> Both the monohydrate and the anhydrous  $\text{Cu}(\text{tmd})_2\text{SO}_4$  have also been prepared.<sup>9</sup>

The complexes  $\text{Ni}(\text{tmd})_3(\text{ClO}_4)_2$ ,  $\text{Ni}(\text{tmd})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ni}(\text{tmd})_2(\text{py})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_2$ ,  $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ , and  $\text{Cu}(\text{tmd})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$  are described in this paper.

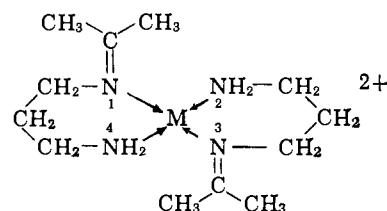
The nickel salts are blue-violet in color, as compared to the mauve of their ethylenediamine analogs, and dissolve in water or methanol to give blue solutions characteristic of nickel(II) bis-diamine salts. The  $\log K_3$  value for the  $\text{Ni}(\text{tmd})_3^{2+}$  ion is 1.23, whereas the corresponding value for the  $\text{Ni}(\text{en})_3^{2+}$  ion is 4.42 and the extensive dissociation of the tris-(1,3-propanediamine) complexes in solution is reflected in these figures.<sup>10</sup> Bis-(1,3-propanediamine)-copper(II) perchlorate was prepared essentially by the method of Pfeiffer<sup>8</sup> and a methanolate,  $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_2 \cdot \text{CH}_3\text{OH}$ , was obtained by recrystallization of this material from methanol. The infrared spectra of the hydrates show strong water bands in the  $3500 \text{ cm}^{-1}$  region and a weaker band at about  $1630 \text{ cm}^{-1}$ . All compounds show bands characteristic of coordinated primary amine groups between  $3225$  and  $3360 \text{ cm}^{-1}$ , at  $3160 \text{ cm}^{-1}$ , and also at about  $1590 \text{ cm}^{-1}$ .

**N-Isopropylidene Complexes.**—When a solution of tris-(1,3-propanediamine)-nickel(II) perchlorate in dry acetone is boiled for a few minutes and allowed to cool, a bright yellow crystalline compound is precipitated. Bis-(1,3-propanediamine)-copper(II) perchlorate yields a purple crystalline compound under the same conditions. These compounds are insoluble in cold water, and in warm water are decomposed to give acetone and the metal diamine complex. They are also insoluble in methanol, ethanol, and acetone but dissolve in dimeth-

ylformamide to give unstable solutions. Analytical data indicate that two acetone molecules have condensed to the primary amine groups of the coordinated ligand and, in the case of nickel, one 1,3-propanediamine molecule is eliminated from the coordination sphere to give a square-planar, diamagnetic complex.



The infrared spectra show bands due to  $-\text{NH}_2$  at  $3300$ ,  $3160$ , and  $1598 \text{ cm}^{-1}$  also present in the starting material, and a new band at  $1665 \text{ cm}^{-1}$  assigned to the  $-\text{C}=\text{N}-$  system. Because these compounds are readily hydrolyzed by water to give acetone only, we have assigned them simple N-isopropylidene structures I and II with possible configurations A, B, and C.

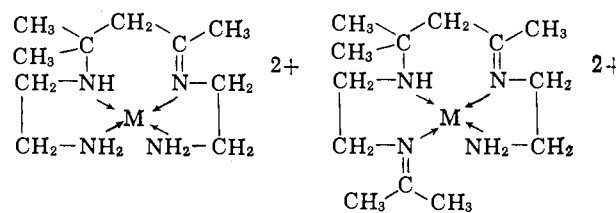


Anion =  $\text{ClO}_4^-$   
 I, M = Ni  
 II, M = Cu

A, isopropylidene groups on N1 and N3  
 B, isopropylidene groups on N1 and N2  
 C, isopropylidene groups on N1 and N4

Because of the unstable nature of the ligand, it is difficult to decide which of the three configurations A, B, or C is the most likely. A model of the complex with structure B shows considerable overlap of the  $-\text{CH}_3$  groups in the adjacent isopropylidene systems and considerable distortion from the plane would result if this configuration were adopted. Of A and C, A is favored, as compounds containing two imine linkages have been shown by X-ray methods to prefer the *trans* position unless forced into a *cis* position by the nature of the ligand.<sup>11</sup>

The structures of I and II differ from those containing two acetone residues III and IV previously described<sup>1-5</sup> in that a bridged quadridentate ligand is not formed.



III, M = Ni  
 IV, M = Cu  
 Anion =  $\text{ClO}_4^-$

V, M = Ni  
 Anion =  $\text{ClO}_4^-$

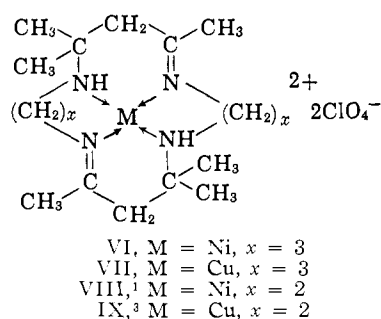
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Compounds III and IV are stable in water and on hydrolysis with 2 *M* acid give mesityl oxide as the only carbonyl product, thus indicating a C<sub>6</sub> bridge in the complex.<sup>5</sup> Compounds I and II, however, show no evidence for C<sub>6</sub> bridges; indeed, their stability is similar to that of other simple aliphatic Schiff base complexes.<sup>12-14</sup> An analogy with compound I occurs in the nickel(II)-ethylenediamine-acetone system, as the compound V, with one N-isopropylidene group, can be formed<sup>1,5</sup> and this is slowly hydrolyzed by water to give acetone and III. The compound II is the first copper(II) complex in this series with an N-isopropylidene group in the ligand.

Previous work in the ethylenediamine series has shown that the production of the cyclic complex VII is diamine catalyzed<sup>15</sup> and by using Ni(en)<sub>2</sub>(py)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·*x*H<sub>2</sub>O only III is formed. However on treating Ni(tmd)<sub>2</sub>(py)<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub>·2H<sub>2</sub>O with acetone in a sealed tube only compound I could be obtained.

**Cyclic Complexes.**—When the metal 1,3-propanediamine perchlorate complexes are allowed to stand in dry acetone at room temperature for about 4 days, a different type of complex is formed. In the case of nickel, the new perchlorate salt forms as large orange-colored crystals as the reaction proceeds, but the new copper salt is more soluble in the acetone solution. It is, however, readily isolated as maroon-colored crystals from the reaction mixture. These compounds are water soluble and moderately stable to hydrolysis. Decomposition with 2 *M* acid and steam distillation of the hydrolyzed solution gives mesityl oxide as the only carbonyl product (isolated as the 2,4-dinitrophenylhydrazine derivative and characterized by the X-ray powder pattern) indicating C<sub>6</sub> bridging units in the complex. The infrared spectrum shows the -NH<sub>2</sub> bands at 3290, 3340, and 1595 cm.<sup>-1</sup>, present in the starting amine complexes, to be absent, and a new band due to the -C=N- system appears at 1660 cm.<sup>-1</sup>. There is also a strong band at about 3230 cm.<sup>-1</sup> due to the coordinated -NH group.<sup>5</sup> Thus these compounds are assigned cyclic structures VI and VII, analogous to the corresponding compounds prepared from the metal ethylenediamine perchlorates, VIII<sup>1</sup> and IX.<sup>3</sup> The position of the double bonds relative to the central metal ion is uncertain and they could be either in the *trans* (as shown) or *cis* configurations. With the configuration shown, VI is 1,5,9,13-tetraza-2,4,4,10,12,12-hexamethylcyclohexadeca-1,9-diene nickel(II) perchlorate and VII is the corresponding copper(II) salt. VI is diamagnetic, supporting the square-planar structure.



These cyclic complexes, although much more stable than those containing N-isopropylidene groups, are less resistant to chemical attack than their ethylenediamine analogs. For example, an aqueous solution of the nickel complex is hydrolyzed by boiling 2 *M* perchloric

acid for about 5 min. and obvious decomposition occurs within 1 min. on addition of ammoniacal dimethylglyoxime solution. Boiling 2 *M* sodium hydroxide solution gives a precipitate of nickel(II) hydroxide and yellow ammonium sulfide forms black nickel(II) sulfide after 15 min. at room temperature. The copper complex shows similar reactivity with acids, bases, and yellow ammonium sulfide solution, but gives no reaction with  $\alpha$ -benzoinoxime or salicylaldehyde reagents. The complexes VIII and IX are unreactive toward all the above reagents. This increased reactivity may be due to the increased strain involved with four six-membered rings surrounding the central metal ion.

**Visible and Ultraviolet Spectra (Table I).**—The visible and ultraviolet spectra of VI are similar to those of the ethylenediamine analog VIII, but the copper complex VII has its absorption maxima shifted to higher wave lengths compared to those of IX. This shift is large enough for a shoulder at 212 m $\mu$  to be observed.

TABLE I  
VISIBLE AND ULTRAVIOLET SPECTRA IN AQUEOUS SOLUTION

	Nickel compounds			Copper compounds			
	—absorption maxima—			—absorption maxima—			
	m $\mu$	cm. <sup>-1</sup> $\times 10^{-3}$	$\epsilon$	m $\mu$	cm. <sup>-1</sup> $\times 10^3$	$\epsilon$	
VI	436	22.8	100	VII	590	16.9	280
	277 <sup>a</sup>	35.1	2,460		286	35.0	6100
	230 <sup>a</sup>	43.5	15,200		212 <sup>a</sup>	47.2	7000
	222	45.0	16,300				
VIII <sup>1</sup>	436	22.8	104	IX <sup>3</sup>	505	19.8	126
	282	35.4	5,400		260	38.4	5400
	238 <sup>a</sup>	42.0	7,900				
	213	47.0	17,300				

<sup>a</sup> This peak is present as a shoulder on the adjacent, more intense, peak.

The low intensity band in the visible region is due to the Laporte forbidden d-d transition. For VI and VIII the band at 436 m $\mu$  ( $\epsilon$  100) is characteristic of the single band of square-planar nickel(II) complexes<sup>16</sup> and the one broad asymmetric band observed in the visible region of VII and IX is characteristic of copper(II) complexes. For VI and VIII, the band at about 280 m $\mu$  is, from its intensity, an "allowed transition" and is probably associated with the  $\pi$ -electrons of the azomethine group conjugated by  $\pi$ -bonding using the d<sub>x<sub>2</sub>-y<sub>2</sub></sub> orbitals of the central nickel atom, as it disappears on reduction<sup>17</sup> (*i.e.*, removal of the azomethine system). Bands in the 210-230 m $\mu$  region with high intensity ( $\epsilon$  16,000) are thought to arise from a charge-transfer transition.

The ultraviolet region of the copper(II) complexes VII and IX shows a band at about 270 m $\mu$  which is unchanged on reduction and has therefore been assigned to a charge-transfer transition while the intense absorption in the region of 200 m $\mu$  in IX is absent in the reduced complex<sup>17</sup> and is thus assigned to the  $\pi$ -electron transition. Similarly the 212 m $\mu$  band in VII is attributed to a  $\pi$ -electron transition. Further details of the spectra for these and the reduced complexes will be published later.

### Experimental

**Tris-(1,3-propanediamine)-nickel(II) Perchlorate, Ni(tmd)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>.**—Nickel(II) perchlorate hexahydrate (36.5 g., 0.1 mole) was dissolved in alcohol (150 ml.) and this solution added dropwise with stirring to a warm solution of 1,3-propanediamine (22.2 g., 0.3 mole) in alcohol (150 ml.). Heat was liberated and the solution turned blue. On cooling and stirring, mauve crystals were readily obtained and, after filtration, the product (40 g., 84%) was dried at 110°.

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*Anal.* Calcd. for  $\text{NiC}_9\text{H}_{30}\text{N}_6(\text{ClO}_4)_2$ : C, 22.5; H, 6.3; N, 17.5; Ni, 12.2. Found: C, 22.6; H, 6.8; N, 17.4; Ni, 12.0.

**Tris-(1,3-propanediamine)-nickel(II) Chloride Dihydrate**,  $\text{Ni}(\text{tmd})_3\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ .—Nickel(II) chloride hexahydrate (24 g., 0.1 mole) was dissolved in ethanol (100 ml.) and 1,3-propanediamine (23 g., 0.3 mole) diluted with an equal volume of ethanol was slowly added. A blue-violet solution was obtained and on cooling in ice the dihydrate (27 g., 70%) was deposited. A sample was prepared for analysis by recrystallization from isopropyl alcohol-water solution.

*Anal.* Calcd. for  $\text{NiC}_9\text{H}_{30}\text{N}_6\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ : C, 27.9; H, 8.9; N, 21.6; Ni, 15.1; Cl, 18.3. Found: C, 28.2; H, 9.1; N, 21.1; Ni, 15.5; Cl, 18.4.

**Bis-(1,3-propanediamine)-bis-(pyridine)-nickel(II) Perchlorate Dihydrate**,  $\text{Ni}(\text{tmd})_2(\text{py})_2(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ .—Nickel(II) perchlorate hexahydrate (9.1 g., 0.025 mole) was dissolved in alcohol (30 ml.) and 1,3-propanediamine (3.7 g., 0.05 mole) added with stirring. The solution was heated to boiling and filtered while hot. Pyridine (9 g., 0.1 mole) was added to the warm blue filtrate and mauve crystals of the product formed on cooling. Ether (10 ml.) was added to complete crystallization. The product (11 g., 85%) was recrystallized from water-ethanol solution containing a few drops of pyridine.

*Anal.* Calcd. for  $\text{NiC}_{16}\text{H}_{30}\text{N}_6(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ : C, 32.0; H, 5.7; Ni, 9.8. Found: C, 31.8; H, 5.5; Ni, 9.9.

**Bis-(N-isopropylidene-1,3-propanediamine)-nickel(II) Perchlorate (I)**.—(a) Tris-(1,3-propanediamine)-nickel(II) perchlorate (8 g.) was added to dry acetone (100 ml.) and the solution heated to boiling. The mauve hexaammine salt dissolved and after 2 min. the solution turned yellow and yellow crystals of the product were precipitated. Boiling was continued for a further 5 min. and the solution cooled and filtered. The yellow crystalline product was washed well with acetone and dried at 100°; yield almost quantitative. The salt is decomposed by warm water and was not recrystallized.

(b) Bis-(1,3-propanediamine)-bis-(pyridine)nickel(II) perchlorate dihydrate (8 g.) was placed in a Carius tube and 50 ml. of acetone added. After 10 min. heating at 100°, the walls of the tube were covered with yellow crystals, and after 12 hr., the product was filtered, washed well with acetone, and air dried; yield almost quantitative.

*Anal.* Calcd. for  $\text{NiC}_{15}\text{H}_{28}\text{N}_4(\text{ClO}_4)_2$ : C, 28.9; H, 5.8; N, 11.5; Ni, 12.0. Found (a): C, 29.0; H, 5.8; N, 11.6; Ni, 12.0. (b): C, 29.2; H, 6.0; N, 11.8; Ni, 12.0.

**1,5,9,13-Tetraza-2,4,4,10,12,12-hexamethylcyclohexadeca-1,9-dienickel(II) Perchlorate (VI)**.—Tris-(1,3-propanediamine)-nickel(II) perchlorate (10 g.) was dissolved in dry acetone (200 ml.) and the mauve solution allowed to stand at room temperature in a stoppered flask. The solution slowly turned yellow-brown and deposited a small quantity of green powder (probably nickel(II) hydroxide). After 4 days, orange crystals of the cyclic complex VI were formed on the walls of the flask. The reaction was stopped after 10 days by decanting the reactant solution from the crystals and washing them twice with hot alcohol to remove acetone polymers. The crystalline product was recrystallized from hot water. A further quantity of the product was isolated from the acetone solution. The deep orange solution was diluted with an equal volume of water, brought to boiling, and filtered from the insoluble material. Decolorizing charcoal was added to the filtrate and the solution boiled until all the acetone had vaporized. After filtration and cooling, orange crystals of the product were formed. The total yield of recrystallized material was 5 g., 40%.

*Anal.* Calcd. for  $\text{NiC}_{18}\text{H}_{36}\text{N}_4(\text{ClO}_4)_2$ : C, 38.3; H, 6.4; N, 9.9; Ni, 10.4. Found: C, 38.6; H, 6.7; N, 9.9; Ni, 10.4.

**Bis-(1,3-propanediamine)-copper(II) Perchlorate**,<sup>8</sup>  $\text{Cu}(\text{tmd})_2(\text{ClO}_4)_2$ .—Copper(II) perchlorate heptahydrate (32.4 g.) was dissolved in alcohol (150 ml.) and slowly added to a stirred solution

of 1,3-propanediamine (15 g.) dissolved in alcohol (100 ml.). A vigorous reaction took place and the solution turned bright blue with the liberation of much heat. As the mixture cooled, blue crystals of the product were readily formed. To complete crystallization, ether (20 ml.) was added to the cool solution. The product was washed with 50-50 alcohol-ether solution and dried at 40°; yield 34 g., 95%. Some of the blue anhydrous perchlorate was placed in an extraction thimble and extracted with refluxing methanol into hot isopropyl alcohol. A blue, crystalline perchlorate methanolate was obtained in the extracting flask. The methanol is only slowly removed by heating at 100°.

*Anal.* Calcd. for  $\text{CuC}_9\text{H}_{18}\text{N}_4\text{Cl}_2\text{O}_8$ : C, 19.0; H, 5.5; Cu, 14.4. Found: C, 19.1; H, 5.7; Cu, 14.4.

**Bis-(1,3-propanediamine)-copper(II) Chloride Monohydrate**,  $\text{Cu}(\text{tmd})_2\text{Cl}_2 \cdot \text{H}_2\text{O}$ .—Anhydrous copper(II) chloride (13.4 g., 0.1 mole) was dissolved in ethanol (90 ml.) and water (10 ml.) and this solution added to 1,3-propanediamine (15 g., 0.201 mole) in ethanol (20 ml.). A bright blue solution was obtained, and on the addition of ether and cooling in ice, blue crystals of the monohydrate (28 g., 93%) crystallized. A sample for analysis was prepared by crystallization from water-methanol-isopropyl alcohol solution.

*Anal.* Calcd. for  $\text{CuC}_9\text{H}_{18}\text{N}_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ : C, 23.9; H, 7.4; N, 18.6; Cl, 23.6; Cu, 21.1. Found: C, 23.8; H, 7.9; N, 18.6; Cl, 23.6; Cu, 20.9.

**Bis-(N-isopropylidene-1,3-propanediamine)-copper(II) Perchlorate (II)**.—Bis-(1,3-propanediamine)-copper(II) perchlorate (8 g.) was treated as in procedure (a) for the nickel complex I. Purple crystals of the product were obtained in an almost quantitative yield. The product was not recrystallized.

*Anal.* Calcd. for  $\text{CuC}_{12}\text{H}_{26}\text{N}_4\text{Cl}_2\text{O}_8$ : C, 29.3; H, 5.7; N, 11.8; Cu, 12.9. Found: C, 29.1; H, 5.7; N, 11.5; Cu, 13.1.

**1,5,9,13-Tetraza-2,4,4,10,12,12-hexamethylcyclohexadeca-1,9-dienecopper(II) Perchlorate (VII)**.—Bis-(1,3-propanediamine)-copper(II) perchlorate (10 g.) was dissolved in dry acetone (200 ml.) and allowed to stand at room temperature in a stoppered flask. The solution turned purple-brown after 1 day and after 5 days was diluted with an equal volume of water, brought to boiling, and filtered from the insoluble material. The acetone was removed by boiling and, after two treatments with decolorizing charcoal, a blue solution with a reddish tinge was obtained. This was concentrated on a water bath and, on cooling, maroon crystals of the product were formed. The product (1.1 g.) was recrystallized from water, washed with alcohol, and dried at 40°. Some 5 g. of unchanged starting material was recovered from the mother liquor; the yield based on bis-(1,3-propanediamine)-copper(II) perchlorate used is 15%.

*Anal.* Calcd. for  $\text{CuC}_{18}\text{H}_{36}\text{N}_4(\text{ClO}_4)_2$ : C, 37.9; H, 6.4; N, 9.8; Cu, 11.1. Found: C, 38.1; H, 6.6; N, 10.2; Cu, 11.2.

**Analysis**.—Methods used were similar to those described previously.<sup>4</sup>

**Spectra**.—The visible and ultraviolet spectra were determined in aqueous solution using a Hilger and Watts H700 Uvispek spectrophotometer. The infrared spectra were determined in mulls, a Perkin-Elmer Model 221 infrared spectrophotometer being used.

**Magnetic Susceptibilities**.—The magnetic susceptibilities of I and VI were measured for the solid by the Gouy method. Both compounds were diamagnetic at 18°.

**Acknowledgments**.—The authors thank Mr. R. Woods of this department for the infrared spectral determinations and Dr. A. D. Campbell of the Otago University for the C and H analyses.