

Curtis N F. Macrocyclic coordination compounds formed by condensation of metal-amine complexes with aliphatic carbonyl compounds.

*Coord. Chem. Rev.* 3:3-47, 1968.

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This review describes coordination compounds of tetraaza amine-imine macrocycles. These are formed by condensation reactions of some di- and tetra-amines, as the nickel(II) or copper(II) complexes, with aliphatic carbonyl compounds. [The *SCI*® indicates that this paper has been cited in over 305 publications.]

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My interest in this topic started with incidental observation, during my PhD thesis project at Auckland University, New Zealand, in 1953, of reactions between ethanediamine nickel(II) complexes and acetone. I was attempting to find a method of preparing diaquabis(ethanediamine)nickel(II) perchlorate faster than slow evaporation of an aqueous solution and tried using a variety of other solvents, including acetone. These were unsuccessful, so I evaporated the solvents off on a steam bath and recrystallized the resulting brown mass by slow evaporation from water. Among the expected large blue crystals were orange and yellow crystals. I was intrigued by this and found that these products formed when bis(ethanediamine)nickel(II) perchlorate was heated with acetone. Another yellow product, formed by reaction of tris(ethanediamine)nickel(II) and acetone, was even more intriguing, as it showed extraordinary chemical inertness, being resistant to concentrated acids, alkalis, and so on.

These simple reactions must have been observed before, but the products are difficult

to crystallize with other anions. Analysis established the stoichiometry of the cations, as formed from two ethanediamine residues, with two, three, and four acetone residues, condensed with loss of two, three, and four moles of water, respectively. These formulae suggested isopropyl imino structures, but known complexes of simple imines were all very susceptible to hydrolysis.

After a period of postdoctoral study, I accepted a faculty position in the Chemistry Department at the Victoria University of Wellington, still intrigued by the enigma represented by these compounds. With the assistance of research students Margaret M. Blight and Don House, the reaction was extended to other amines, to other carbonyl compounds, and to copper(II). The ethanediamine/acetone compounds of nickel(II)<sup>1</sup> and copper(II)<sup>2</sup> were reported, with the imine structures proposed, with reservations because of the resistance to hydrolysis. We sought alternative structures, and House suggested isomers, with the acetone residues joined to form an amine-imine chelate ring linking two amine groups. Isolation of mesityl oxide from acid hydrolysis of the "two acetone" product, mesityl oxide plus acetone from the "three acetone" product, and mesityl oxide from cyanide decomposition of the "four acetone" product provided confirmation.

The macrocyclic nature of the ligand present for this cation, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, was now apparent, as we at last recognized that we had a bull by the tail, and the macrocyclic structure was proposed<sup>3</sup> and the system extended.<sup>4</sup>

These compounds were the first reported in the now very extensive area of nonpyrrole azamacrocyclic ligands, and are still probably the most easily prepared macrocyclic complexes. I still find interest in them, 35 years later.<sup>5</sup> The review is widely cited as a historical introduction to the azamacrocyclic ligands<sup>6</sup> and by people using the compounds.

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3. Curtis N F & House D A. Structure of some aliphatic Schiff base complexes of nickel (II) and copper (II). *Chem. Ind.—London* 1961:1708-9. (Cited 40 times.)
4. Curtis N F. Some metal-ion complexes with ligands formed by reaction of amines with aliphatic carbonyl compounds. Part I. Nickel(II) and copper(II) complexes formed by the diaminoethane-acetone reaction. *J. Chem. Soc. Dalton Trans.* 1972:1357-61. (Cited 35 times.)
5. Curtis N F & Osvath S R. Kinetics of acid-promoted dissociation of diamine-diimine macrocycle complex cations with nickel(II) and copper(II). *Inorg. Chem.* 27:305-10, 1988.
6. Curtis N F. Other polyaza macrocycles. (Wilkinson G, Gillard R D & McCleverty J A, eds.) *Comprehensive coordination chemistry: the synthesis, reactions, properties & applications of coordination compounds. Volume 2: ligands.* Oxford, UK: Pergamon Press, 1987. p. 899-914.

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