

Curtis N F & Curtis Y M. Some nitrate-amine nickel(II) compounds with monodentate and bidentate nitrate ions. *Inorg. Chem.* 4:804-9, 1965.

[Department of Chemistry, Victoria University of Wellington, New Zealand]

The preparations and properties of nitrate complexes of nickel(II) with the cyclic amines *C-meso*- and *C-racemo*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane and with linear diamines, triamines, and tetramines are reported. The fundamental, overtone and combination bands of the infrared spectrum characteristic of unidentate and bidentate coordination by the nitrate ion are characterized. [The *SCI*® indicates that this paper has been cited in over 440 publications.]

Infrared Spectra of Nitrate Coordinated to Nickel(II)

Neil F. Curtis
Department of Chemistry
Victoria University of Wellington
Wellington
New Zealand

January 10, 1989

This study of the infrared spectra of nitrate complexes of nickel(II), developed from ongoing research on azamacrocyclic complexes of the later transition metals, started by the discovery of the condensation reaction between tris(ethanediamine)-nickel(II) perchlorate and acetone, which yields the azamacrocyclic cation (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II).¹ Reduction of the imine groups produces *C-meso* and *C-racemo* isomers of the cyclic amine cation (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II). These are coordinated by a variety of anions to form octahedral, triplet ground state compounds. The isomers have quite different steric properties; the *C-meso* isomer, with one axially oriented methyl substituent on each side of the "molecular plane," usually forms *trans*-diacido derivatives, while the *C-racemo*

isomer, which has both of these groups on the same side of the "plane," usually forms *cis* derivatives, with the macrocycle in folded coordination, particularly when an anion can act as a chelate and can occupy both "additional" coordination sites. This stereochemical difference permits easy separation of the isomers, as the *C-racemo* isomer derivatives with chelates are often much less soluble than those of the *C-meso* isomer with *trans* geometry. Preparations of many of these derivatives are facilitated by the extreme resistance of the nickel(II) cyclic amine cations to acid hydrolysis.

It was apparent that the isomeric cations provided a method of characterizing anionic ligands in bidentate and unidentate coordination modes, particularly by infrared spectroscopy; spectra of tetrahydroborato,² oxalato,³ and acetato⁴ compounds (among others) have been described.

At that time my wife, Yvonne, was working in the Chemistry Department, and we decided to extend the study to the nitrate compounds, using the compounds of the isomeric macrocyclic cations as examples of unidentate and bidentate coordination modes of the nitrate ion, and applying the assignments of the infrared spectra to nitrate compounds of other amines coordinated to nickel(II). A disadvantage of the macrocyclic complex cations for this purpose was their complex infrared spectrum in the "fingerprint" region, which made assignment of weak bands in this spectral region arising from other ligands difficult. Yvonne persisted with the spectra of the nitrate complexes and eventually teased out the assignments, making use of the often-ignored weaker overtone and combination mode bands in the 2500-1600 cm⁻¹ spectral region.

Others have found the paper useful because it provides a method of distinguishing between unidentate and bidentate coordination by the nitrate ion in a variety of environments.⁵

1. Curtis N F. Macrocyclic coordination compounds formed by condensation of metal-amine complexes with aliphatic carbonyl compounds. *Coord. Chem. Rev.* 3:3-47, 1968. (Cited 320 times.) [See also: Curtis N F. Citation Classic. *Current Contents/Engineering, Technology & Applied Sciences* 19(36):14, 5 September 1988 and *CC/Physical, Chemical & Earth Sciences* 28(36):14, 5 September 1988.]
2. ———. Amine-oxalate complexes of nickel(II): preparations and infrared spectra. *J. Chem. Soc.* 1963:4109-15. (Cited 85 times.)
3. ———. Borohydride derivatives of some nickel(II) cations. *J. Chem. Soc.* 1965:924-31. (Cited 45 times.)
4. ———. Some acetato-amine complexes of nickel(II), copper(II) and zinc(II). *J. Chem. Soc. A* 1968:1579-84. (Cited 145 times.)
5. Sacconi L, Mani F & Bencini A. Nickel. (Wilkinson G, Gillard R D & McCleverty J A, eds.) *Comprehensive coordination chemistry: the synthesis, reactions, properties, and applications of coordination compounds. Volume 5: late transition elements.* Oxford, England: Pergamon Press, 1987. p. 1-347.

1A-14