The Crystal Structure of an Oxime Complex of Nickel(II) with Oximino Oxygen-to-Nickel Bonding in a Chelate Ring

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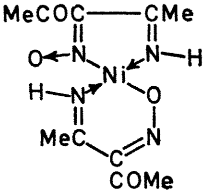
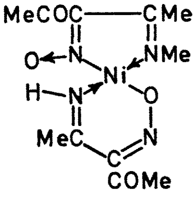
Summary The *X*-ray crystal structure of (4-methyliminopentane-2,3-dione 3-oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II) shows that the former ligand is chelated to the nickel atom *via* its oximino-nitrogen atom, while the latter is chelated *via* its oximino-oxygen atom.

WE have presented evidence[1] that the red complex, bis-(4-iminopentane-2,3-dione 3-oximato)nickel(II) has the structure (I) in which there occur two modes of attachment


(I)


(II)

of the oxime group of the ligand to the same metal atom in each molecule. We have now synthesized and obtained the *X*-ray diffraction structure of the related mixed-ligand complex, (4-methyliminopentane-2,3-dione 3-oximato)(4-iminopentane-2,3-dione 3-oximato)nickel(II), [structure (II)]. This is the first example of a metal chelate complex in which an oxime ligand has been shown by *X*-ray diffraction to involve chelation to the central metal atom *via* oximino oxygen-to-metal bonding rather than oximino nitrogen-to-metal bonding.

The mixed-ligand complex was prepared by the reaction of nickel acetate (10 mmole), potassium nitrite (60 mmole), methylamine hydrochloride (50 mmole), and pentane-2,4-dione (20 mmole) in 1 : 5 ethanol–water (60 ml) at room temperature with stirring for 2 h, followed by the addition of ammonium hydroxide (4 ml, d 0·880) to precipitate the crude product on standing. The complex was purified by recrystallization from benzene–petroleum as orange-red needles. Molecular ion composition $C_{11}H_{16}N_4NiO_4$ as obtained by high-resolution mass spectrometry, was confirmed by satisfactory microanalyses. Suitable crystals for *X*-ray analysis were obtained by slow crystallization at room temperature from chloroform–petroleum and were monoclinic with unit-cell parameters $a = 8{\cdot}468$, $b = 19{\cdot}953$, $c = 8{\cdot}419$ Å, $\beta = 107{\cdot}66°$, giving a volume of 1355 Å^3 for four molecules in the unit cell. The structure was solved by Patterson methods and refined by the method of least squares, using the program ORFLS,[2] with anisotropic temperature factors. All hydrogen atoms were found but their positional parameters only were included in the refinement. The final agreement factor was 0·083.

The Figure is a projection roughly normal to the plane of the molecule. Hydrogen atoms have been omitted with the exception of the imino-hydrogen atom, represented as a small sphere, to show its position relative to that of the oximino-oxygen atom and to indicate the strength of possible hydrogen bonding. The molecule is essentially planar with the planes of the five- and six-membered rings making an angle of 2·3° with each other.

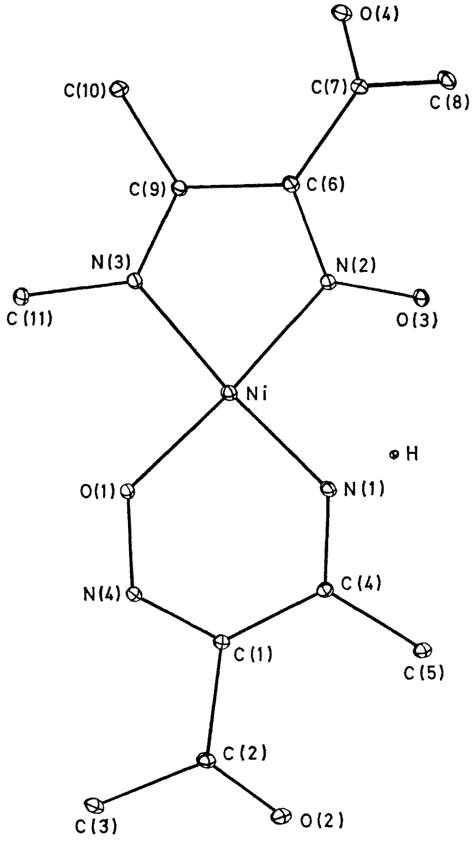


FIGURE. *Pertinent distances (in Å) and angles are* Ni–N(1) 1·81; Ni–N(2) 1·88; Ni–N(3) 1·89; Ni–O(1) 1·81; N(1)–H 0·90; N(2)–O(3) 1·26; Ni–N(1)–H 109°; Ni–N(2)–O(3) 122°; N(1)–Ni–O(1) 93°; O(1)–Ni–N(3) 92°; N(2)–Ni–N(3) 83°; N(1)–Ni–N(2) 92°.

Oximes have been used widely in the sequestration of metals and the relationship between geometrical isomerism and chelating ability for oximes of vicinal diketones has been known for several years.[3] In general, it has been accepted that the most stable metal complexes are formed when the chelate rings involve oximino nitrogen-to-metal bonding, based on the known geometrical configuration of the ligand molecule. Previous *X*-ray analyses of metal complexes of dioximes[4] and mono-oximes[5] have revealed only the presence of chelate rings involving oximino nitrogen-to-metal bonding. In some cases,[3] metal complexes have been formed from other geometrical isomers of the oximes for which structures involving oximino oxygen-to-metal coordination in the chelate rings are sterically possible, but the instability or insolubility of these complexes has impeded attempts to substantiate the structures by *X*-ray analysis.

One of us (J. F. McC.) acknowledges the use of equipment supplied by funds from the Australian Research Grants Committee.

(*Received, July* 21*st*, 1971; *Com.* 1264.)

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