Communications

Crystal & Molecular Structure of (3,10-dihydroxyimino-4,9-dimethyl-5,8-diazadec-4,9-diene-2,11-dionato)nickel(II) (α-Form) — A Rare Example of Intra-ligand Chelate Linkage Isomerism

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Nickel(II) complex of ethylene-bis-isonitrosoacetylacetoneimine has been synthesised in three crystalline forms and characterised by infrared and FT PMR spectroscopy. The X-ray structure of the α-form has been solved from 1237 visually estimated intensity data and refined to a R-value of 0.14. Ni(II) has a square planar structure, coordinated through two ethylenediamine nitrogens, one isonitroso nitrogen and one isonitroso oxygen. The structure provides a rare example wherein the ambidentate hydroxyimino group of the same homogeneous ligand exhibits dual mode of coordination to the same metal ion.

STUDIES on the coordination compounds of monovalent bidentate, 3-hydroxyiminoo-4-imino-2,3-pentanedione (HHPI) and the related ligands are of current interest, since the hydroxyimino group (>C = NOH) can coordinate to a metal ion through either nitrogen or oxygen producing chelate linkage isomeric complexes 1-3. For example, HHPI reacts with nickel acetate forming a diamagnetic complex, Ni(HPI) (HPI'), in which HPI coordinates through hydroxyimino-nitrogen, while HPI co-ordinates through hydroxyimino-oxygen1. A structure of this type has been confirmed in the related molecule (4-methyliminopentane-2,3-dione-3-oximato) (4-iminopentane-2,3-dione-3-oximato) nickel (II) by X-ray crystal structure analysis4. To examine further the coordination behaviour of the ambidentate hydroxyimino group we have extended these studies to tetradentate ligands. This communication reports the synthesis, spectra and molecular structure of the title compound. The compound was first prepared by Masuda et al.5 and assigned structure(I). Iyengar4 on a reinvestigation favoured structure(II). These results were mainly based on IR data. In the present studies, spectroscopy as well as X-ray diffraction have been employed to establish the structure unambiguously.

The complex was prepared by three different methods.
(i) This is essentially the same as Masuda’s method, giving red crystals of the complex (α-form).
(ii) To a mixture of nickel acetate tetrahydrate (0.001 mol), sodium nitrite (0.06 mol) and acetic acid (3 ml) in acq. methanol (80%, 100 ml), a mixture of acetylacetone (0.002 mol) and ethylene-diamine (0.003 mol) in methanol was added slowly with constant stirring. The resulting reaction mixture was maintained at room temperature for 6-8 days with occasional shaking. The orange red crystals (β-form) obtained were filtered, washed with methanol and air-dried, yield 90%.

(iii) The principle of template synthesis was made use of in this method. A mixture of tris(ethylenediamine) nickel(II) chloride tetrahydrate (0.001 mol) and isonitrosoacetylacetone (0.002 mol) in methanol-chloroform (2:1 by volume, 100 ml) was refluxed on a steam-bath for 30-40 hr. The orange-yellow plate-like crystals (γ-form) deposited were filtered and washed with chloroform; yield 80%.

Crystals suitable for the X-ray analysis could only be obtained for the α-form by crystallizing from a large excess of chloroform. Intensity data were obtained by the multiple film equi-inclination Weissenberg technique using CuKα radiation. The intensities of 1237 reflections were estimated visually. The positional parameters of the (non-hydrogen) atoms were determined by Patterson and Fourier methods. The structure has been refined by least squares with anisotropic temperature factors for the atoms to a conventional R value of 0.14.

The FT PMR spectrum of the complex (α-form only) was recorded on a Varian—FT 100 MHz spectrometer with a pulse delay of 100 µ sec. The IR spectra in nujol were obtained on a Carl-Zeiss UR-10 automatic double beam spectrometer fitted with LiF, NaCl and KBr prisms.

The title compound, obtained in three different crystalline forms (α, β and γ) depending upon the method of preparation, gave the same chemical analyses. The β and γ forms have very low solubility in the common organic solvents whereas the α-form is soluble to some extent. All are diamagnetic and decompose above 200°C.

In view of the dual mode of coordination of the hydroxyimino group, three structures (I, II, III) could be expected for the complex. The solid state
IR spectra of all the three forms of the complex in the range 400-1800 cm\(^{-1}\) are virtually identical except for small shifts in the band positions. This suggests that all the three forms are crystalline modifications having the same molecular structure. Two intense vibrational bands are observed in the region 1660-1700 cm\(^{-1}\), which are in the region expected for the non-coordinated acetyl v(CO). The absorption bands around 1160 and 1200 cm\(^{-1}\) can be assigned to two different types of coupled v(NO), the former due to O-coordination and the latter to N-coordination. The FT PMR spectrum of the a-form in CDCl\(_3\) shows two singlet signals at 2.08 and 2.21, which are assigned to two methyl resonance signals. The complex multiplet centred at 1.30 shows integrated intensity corresponding to two methyl groups and is assigned to the methyl protons in the vicinity of the ethylene bridge. The PMR as well as IR data could be accounted for by postulating the structure (III) rather than I and II.

Crystal data — C\(_{12}\)H\(_{16}\)N\(_4\)O\(_4\)Ni, M = 339, triclinic P\(_1\); \(a = 7.708(2)\), \(b = 7.793(3)\), \(c = 11.940(3)\) \(\AA\), \(\alpha = 100.4(2)^\circ\), \(\beta = 99.6(2)^\circ\), \(\gamma = 90.03(2)^\circ\), \(U = 695 \text{ \AA}^3\), \(Z = 2\), \(D_m = 1.60 \text{ g/cm}^3\) (by flotation), \(D_e = 1.62 \text{ g/cm}^3\).

A view of the molecule down \(a\) axis is shown in Fig. (1). It can be seen that the tetradoenate ligand coordinates to Ni(II) through two nitrogens of the ethylenediamine and one of the isonitroso nitrogens. A square planar geometry is completed by coordination through an isonitroso oxygen producing the hybrid ring structure (III). The coordinating distances and angles at Ni(II) are given in Fig. 1. The Ni-N(15) distance is longer than normal. This may be due to the inaccuracy in the positional parameters of N(15) due to abnormally high thermal parameters. Ni(II) is virtually in the plane of the four coordinating atoms. The five- and six-membered chelate rings, Ni—N(15)—C(3)—C(4)—N(5) and Ni—N(8)—C(9)—C(10)—N(14)—O(3), are essentially planar. The ethylene bridge is \textit{trans} with respect to the coordination plane. C(6) and C(7) being out of the plane by \(-0.13\)\(\AA\) and \(+0.15\)\(\AA\) respectively. The two acetyl groups are inclined by 9° and 36° respectively, with respect to the five- and six-membered rings to which they are attached. In the crystal the closest Ni—Ni separation of 3.49 \(\AA\) in symmetry-relat ed molecules suggests negligible metal-metal interaction. This distance may be compared with 3.245 \(\AA\) in/bis (dimethylglyoximato)-nickel(II) where weak interaction has been postulated.

We believe the present structure provides a rare example wherein the ambidentate hydroxyimino group of the same homogeneous ligand exhibits dual mode of coordination to the same metal ion. This phenomenon may be called intra-ligand chelate linkage isomerism of the hydroxyimino group, as compared to inter-molecular chelate linkage isomerism identified earlier in analogous compounds. It is rather difficult to explain the peculiar structural configuration adopted by Ni(II) in this complex. The preferred structure may be due to electronic and/or steric effects. The latter effect appears to be dominant in the present case.

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References