

The X-Ray Crystal Structure of Bis(glycinohydroxamato)nickel(II). A Novel Co-ordination of Nickel by a Hydroxamic Acid *via* the Nitrogen Atom of the NHOH Group

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X-Ray crystallography shows that glycinohydroxamic acid (gha) forms a bis complex with nickel(II), Ni(gha)₂, which is the first example of co-ordination of a transition metal by a hydroxamic acid *via* the nitrogen atom of the NHOH group.

Over the past decade, interest in complexes of both monohydroxamic acids, RCON(R')OH,^{1,2} and naturally occurring trihydroxamic acids³ has increased greatly. X-Ray crystallographic studies of tris(benzohydroxamato)iron(III) dihydrate,⁴ tris(benzohydroxamato)chromium(III),⁵ tetrakis(*N*-isopropyl-3,3-dimethylbutanohydroxamato)thorium(IV),⁶ and tetrakis(*N*-phenylbenzohydroxamato)hafnium(IV)⁷ show co-ordination of the central metal atom by the oxygen atoms of the ligand. Analogous co-ordination through oxygen and sulphur atoms occurs in tris(*N*-methylthiobenzohydroxamato)cobalt(III), -chromium(III), -iron(III), and -manganese(III).⁸ We report the structure of bis(glycinohydroxamato)nickel(II) which is the first example, to our knowledge, of co-ordination of a transition metal by a hydroxamic acid *via* the *nitrogen* atom of the NHOH group rather than through the oxygen atom. Evidence that urease contains small quantities of nickel⁹ and inhibition of urease activity by both monohydroxamic acids and amino-hydroxamic acids¹⁰ prompted our studies of their nickel complexes.

Proton-ligand stability constants of glycinohydroxamic acid NH₂CH₂CONHOH (gha)¹¹ and stability constants and species distribution for the nickel(II)-gha system have been determined by the Sarkar-Kruck method.¹² In the pH region, 5.6–6.2, the Ni(gha) species predominates whereas in the region 6.2–8.6, the Ni(gha)₂ species predominates with evidence at higher pH for deprotonated species such as Ni(H₋₁gha)₂ and Ni(H₋₂gha)₂. The log stability constants for Ni(gha) and Ni(gha)₂ are 6.8 and 13.50, respectively, measured in 0.15 M NaCl solution at 25 °C. Proton liberation reaches a maximum of 3.6 at pH 7.0 when the Ni(gha)₂ species predominates but since the p*K*₂ of free gha is 7.5, the proton liberation value indicates co-ordination of both the amino- and the deprotonated(NHO⁻)-hydroxamato group to

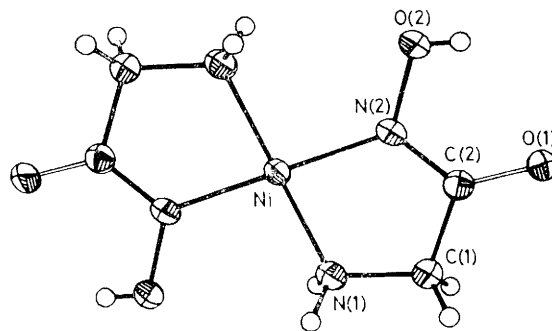


Figure 1. The molecular structure of Ni(gha)₂. Important interatomic distances: Ni–N 1.906(2), Ni–N(2) 1.846(2), N(1)–C(1) 1.481(4), C(1)–C(2) 1.507(4), C(2)–O(1) 1.252(3), C(2)–N(2) 1.307(3), N(2)–O(2) 1.414(3) Å; angles: N(1)–Ni–N(2) 83.9(1), Ni–N(1)–C(1) 112.6(2), N(1)–C(1)–C(2) 109.8(2), C(1)–C(2)–N(2) 112.2(2), C(2)–N(2)–Ni 120.7(2), Ni–N(2)–O(2) 122.9(2), O(2)–N(2)–C(2) 116.1(2), N(2)–C(2)–O(1) 125.6(2), O(1)–C(2)–C(1) 122.2(2)°.

nickel(II). Direct synthesis at pH 6.9 gave red diamagnetic† crystals of Ni(gha)₂ (yield 95%), m.p. 218 °C (decomp.). The i.r. spectrum (KBr disc) in the 3000–3500 cm⁻¹ region is similar to that of bis(glycinato)nickel(II)¹² supporting co-ordination by the amino group whilst the 650–950 cm⁻¹ region is consistent with co-ordination by the NHO⁻ group.¹ The absence of any shift in carbonyl frequency between the complex and free ligand argues against co-ordination by the

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carbonyl group although in 1:1 mixtures of Ni²⁺ and gha in D₂O, concentration-dependent shifts occur probably owing to intermolecular hydrogen bonding. The structure of Ni(gha)₂ is shown in Figure 1.

Crystal data: C₄H₁₀N₄O₄Ni, *M* = 236.8, monoclinic, space group *P*2₁/*c*, *a* = 5.360(1), *b* = 7.315(4), *c* = 10.194(4) Å, β = 96.57(3)°, *U* = 397.0(3) Å³, *Z* = 2, *D*_c = 1.98 g cm⁻³, *F*(000) = 244 electrons, μ(Mo-*K*_α) = 24.3 cm⁻¹. Intensity data were recorded on a Nicolet R3m diffractometer (graphite-monochromated Mo-*K*_α X-radiation, λ = 0.71069 Å), in the range 3 ≤ 2θ ≤ 60° with 855 out of 1354 reflections having *F* ≥ 5.0σ(*F*). The structure was solved by the heavy atom method and refined by the blocked-cascade least-squares techniques using the SHELXTL program package¹³ to the current *R* of 0.0275.‡

The geometry of the bis(glycinohydroxamato)nickel(II) complex is shown in Figure 1. The co-ordination about the central Ni^{II} atom is square planar with four nitrogen atoms of the two glycinohydroxamato ligands occupying the four co-ordination sites, with an inversion centre on the nickel. Except for the hydrogens, the complex is planar with a maximum deviation from the molecular plane of 0.07 Å. The bidentate glycinohydroxamato ligand is co-ordinated to the nickel(II) *via* the amino groups, NH₂, and surprisingly *via* the nitrogen atom of the NOH⁻ group. The distances and angles of the chelate group show no unexpected features except in the hydroxamato group, NOHCO, where the length of the N(2)–C(2) bond [1.307(3) Å] is considerably shorter than that observed for a single C–N bond in glycine [1.474(5) Å]¹⁴ or in the present structure for the N(1)–C(1) bond [1.481(4) Å]. The N(2) atom displays bond angles consistent with sp² hybridization. These two features indicate considerable π-electron delocalization from the nitrogen, N(2), to the carbonyl group. The two metal–ligand distances Ni–N(amino, NH₂) 1.906(2) Å and Ni–N(NOH⁻) 1.846(2) Å are not equal and can be compared to analogous distances found in two disodium triglycylglycinatonickelate(II) hydrates with square planar co-

ordination about Ni^{II},¹⁵ where they average 1.924 and 1.84 Å [Ni–N(peptide)], respectively. The observed Ni–N distances are shorter than those in octahedral Ni^{II} complexes with similar ligands¹⁶ and are thus consistent with a 4-co-ordinate structure. The complexes in the Ni(gha)₂ structure are held together by a network of intermolecular hydrogen bonds. The hydrogen atoms of the NOH⁻ groups are involved as donors to oxygen atoms on the carbonyl groups with average H·····O distances of 2.11(4) Å. In view of the solution i.r. spectra and species distribution, it appears probable that the above structure persists in solution.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.