

***cis*-Addition to a Square-Planar Ni Complex: Structure of Bis(oxamide oxime)-bis(propiolato)nickel(II)–Bis(dimethylformamide)–Water,
[Ni(C₂H₆N₄O₂)₂(C₃HO₂)₂].2C₃H₇NO.H₂O**

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Abstract. $M_r = 597.2$, triclinic, $P\bar{1}$, $a = 10.260$ (3), $b = 10.719$ (3), $c = 13.495$ (3) Å, $\alpha = 67.43$ (2), $\beta = 88.35$ (2), $\gamma = 79.56$ (2)°, $V = 1346.4$ Å³, $Z = 2$, $D_x = 1.47$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 7.9$ cm⁻¹, room temperature, $F(000) = 624$, final $R = 0.076$ for 1134 observed reflections. The octahedral title complex resulted from *cis*-addition of propiolic (propynoic) acid, formed from acetylenedicarboxylic acid by decarboxylation, to square-planar bis(oxamide oximate)-nickel(II).

Introduction. The square-planar neutral Ni^{II} complex of oxamide oxime, HON=C(NH₂)–C(NH₂)=NOH (diaminoglyoxime, oaoH₂), Ni(oaoH)₂ (Endres, 1979), adds organic acids HX to form *cis*-octahedral Ni(oaoH₂)₂X₂ complexes (Endres, 1983). With polycarboxylic acids the formation of polymers has been observed. In the following we describe the results obtained with acetylenedicarboxylic acid. Besides adduct formation a reaction with the amino groups seemed possible, by analogy with the reaction of the dimethyl ester of acetylenedicarboxylic acid with *o*-phenylenediamine to substituted 1,4-benzodiazepine derivatives (Heindel, Fish & Lemke, 1968). We obtained two products: a not well characterized and probably polymeric adduct of acetylenedicarboxylic acid, and the title compound. The latter resulted from a decarboxylation of acetylenedicarboxylic acid.

Experimental. 5 mmol of acetylenedicarboxylic acid dissolved in 20 ml dimethylformamide (dmf) at 353 K. Solid Ni(oaoH)₂ added portionwise, dissolved with gas evolution. When ca 1.5 mmol of the Ni complex had been added, it no longer dissolved. Solution filtered; deep-green filtrate concentrated to 1/10 of original volume by slow evaporation; dark-green crystals of the title compound formed on cooling in refrigerator. They decompose in air within a few hours, probably due to loss of solvent. The IR spectrum shows a weak but sharp band for the C≡C stretching frequency at 2100 cm⁻¹.

Block-like crystal (0.008 mm³) mounted inside a glass capillary. Lattice parameters from setting angles of 25 reflections (Syntex R3, monochromatic Mo $K\alpha$ radiation). Rapid θ – 2θ data collection (min. 2θ scan speed 4° min⁻¹), $2\theta \leq 50^\circ$, 4741 reflections measured, 1134 observed independent reflections with $I > 2.5\sigma(I)$, hkl range –10, –11, 0 to 11, 12, 14, no equivalent reflections measured, two check reflections at intervals of 200, intensity variation $\pm 3.9\%$. Empirical absorption correction using ψ scans of four reflections, min. transmission 0.72 (max. = unity). Ni position from Patterson map, other non-H atoms from Fourier map. Not all H evident on difference Fourier map: those of the dmf methyl groups calculated and refined as rigid groups, other H atoms not included. Ni refined anisotropically, other atoms isotropically. Refinement by 'cascade-matrix' least squares based on F , $w = 1/\sigma^2(F)$, $R_w = 0.064$, $R = 0.076$, $S = 1.65$; max. shift/error 0.06. Largest features in final difference Fourier map +0.51 and –0.43 e Å⁻³. SHELXTL program system (Sheldrick, 1981) on a Nova 3 computer, plots on a Tektronix plotter, scattering factors from *International Tables for X-ray Crystallography* (1974), anomalous dispersion included.

Discussion. Atomic coordinates are listed in Table 1,* bond distances and angles in the Ni complex in Table 2. The complex molecule is shown in Fig. 1. Ni is octahedrally coordinated by two oxamide oxime chelate ligands and two propiolate anions in *cis* positions. The latter result from decarboxylation of acetylenedicarboxylic acid. From the observation that addition of Ni(oaoH)₂ to the solution of the acid is accompanied by gas evolution, it may be concluded that the decarboxylation occurs in the ligand sphere of Ni. It is

* Lists of structure factors, anisotropic thermal parameters for Ni, rigid-group-refined H coordinates, and bond lengths and angles in the dmf molecules have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38761 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

thermally induced and does not take place at ambient temperature. Although the H atoms could not be detected, it is certain that the oaoH₂ ligands are present as neutral molecules and the carboxylic acid as anions, as the oxime groups are less acidic than the carboxylic acid. This in accord with other structures of this type, where H positions had been determined (Endres, 1983).

The important point in this structure determination is that the two anions *X* occupy *cis* positions in the octahedral [Ni(oaoH₂)₂X₂] molecule. Formation of *trans*-octahedral complexes has never been observed in any [Ni(oaoH₂)₂X₂] complexes investigated so far (Endres, 1983). Hence the generalized textbook formulation: 'For any square complex NiL₄, equilibria with additional ligands *L'* must in principle exist... in most cases equilibria strongly favour the six-coordinate species that have *trans* structures' (Cotton & Wilkinson, 1980) must be treated with caution. The structure of an analogous *cis*-octahedral Co^{II} complex, formed by addition of trifluoroacetic acid to bis(dimethylglyoximate)cobalt(II), has recently been reported (Alcock, Atkins, Curzon, Golding & Sellars, 1980).

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Table 1. Atom coordinates ($\times 10^4$) and isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ni	-103 (3)	-607 (2)	7622 (2)	24 (1)*
N(1)	466 (14)	-2550 (13)	7492 (11)	38 (5)
N(2)	1405 (14)	-1647 (13)	8811 (10)	39 (4)
O(1)	-340 (11)	-3162 (11)	7055 (8)	31 (3)
O(2)	2166 (11)	-1063 (10)	9316 (8)	36 (3)
C(1)	1094 (16)	-3495 (15)	8366 (12)	21 (5)
C(2)	1858 (18)	-2911 (16)	8946 (13)	34 (5)
N(3)	1056 (13)	-4858 (12)	8738 (10)	29 (4)
N(4)	3034 (13)	-3722 (13)	9552 (10)	35 (4)
N(5)	-1675 (13)	-1414 (13)	8562 (10)	33 (4)
N(6)	-1732 (14)	-39 (13)	6527 (11)	32 (4)
O(3)	-1586 (10)	-2358 (10)	9643 (8)	29 (3)
O(4)	-1852 (11)	890 (10)	5458 (9)	40 (4)
C(3)	-2752 (17)	-1438 (16)	8060 (13)	34 (5)
C(4)	-2866 (18)	-408 (16)	6887 (13)	29 (5)
N(7)	-3728 (14)	-2146 (13)	8471 (11)	46 (5)
N(8)	-3965 (12)	29 (12)	6266 (10)	27 (4)
O(5)	1406 (11)	232 (10)	6611 (8)	32 (3)
C(5)	1382 (18)	1129 (18)	5698 (14)	51 (6)
O(6)	334 (11)	1662 (11)	5052 (9)	46 (4)
C(6)	2591 (18)	1753 (17)	5276 (14)	34 (5)
C(7)	3539 (20)	2273 (19)	4903 (15)	54 (6)
O(9)	-659 (11)	1249 (11)	7803 (8)	32 (4)
C(9)	-264 (18)	1779 (18)	8399 (14)	38 (6)
O(10)	710 (11)	1317 (10)	9052 (9)	39 (4)
C(10)	-1024 (16)	3176 (16)	8220 (13)	32 (5)
C(11)	-1682 (18)	4257 (18)	8086 (14)	51 (6)
O(13)	5973 (12)	3465 (12)	3934 (10)	69 (5)
C(13)	6985 (19)	3949 (19)	3944 (16)	60 (7)
N(9)	7258 (18)	4126 (16)	4872 (14)	65 (6)
C(14)	6521 (21)	3722 (23)	5839 (17)	100 (9)
C(15)	8509 (22)	4499 (21)	4964 (19)	115 (10)
O(14)	4470 (13)	3633 (12)	9305 (10)	61 (4)
C(16)	3960 (20)	3253 (18)	8664 (16)	59 (7)
N(10)	4497 (16)	2219 (15)	8434 (12)	50 (5)
C(17)	5768 (21)	1456 (24)	8767 (21)	138 (11)
C(18)	3819 (21)	1737 (23)	7747 (18)	106 (9)
O(15)	6075 (11)	1592 (11)	2965 (9)	50 (4)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized *U_{ij}* tensor.

Table 2. Bond lengths (\AA) and angles ($^\circ$) in the Ni complex

Ni-N(1)	2.131 (15)	Ni-N(2)	2.087 (13)
Ni-N(5)	2.121 (14)	Ni-N(6)	2.105 (15)
Ni-O(5)	2.124 (11)	Ni-O(9)	2.073 (12)
N(1)-O(1)	1.409 (21)	N(1)-C(1)	1.314 (17)
N(2)-O(2)	1.414 (21)	N(2)-C(2)	1.293 (22)
C(1)-C(2)	1.486 (28)	C(1)-N(3)	1.358 (20)
C(2)-N(4)	1.418 (20)	N(5)-O(3)	1.416 (14)
N(5)-C(3)	1.322 (24)	N(6)-O(4)	1.397 (15)
N(6)-C(4)	1.316 (24)	C(3)-C(4)	1.536 (24)
C(3)-N(7)	1.344 (23)	C(4)-N(8)	1.325 (21)
O(5)-C(5)	1.235 (18)	C(5)-O(6)	1.301 (20)
C(5)-C(6)	1.509 (26)	C(6)-C(7)	1.210 (27)
O(9)-C(9)	1.260 (26)	C(9)-O(10)	1.247 (20)
C(9)-C(10)	1.489 (24)	C(10)-C(11)	1.181 (24)
N(1)-Ni-N(2)	76.3 (6)	N(1)-Ni-N(5)	87.1 (6)
N(2)-Ni-N(5)	96.6 (5)	N(1)-Ni-N(6)	92.1 (6)
N(2)-Ni-N(6)	166.1 (6)	N(5)-Ni-N(6)	74.8 (5)
N(1)-Ni-O(5)	92.8 (5)	N(2)-Ni-O(5)	86.2 (5)
N(5)-Ni-O(5)	177.1 (5)	N(6)-Ni-O(5)	102.3 (5)
N(1)-Ni-O(9)	178.1 (5)	N(2)-Ni-O(9)	102.4 (5)
N(5)-Ni-O(9)	91.6 (5)	N(6)-Ni-O(9)	88.9 (5)
O(5)-Ni-O(9)	88.5 (4)	Ni-N(1)-O(1)	125.4 (9)
Ni-N(1)-C(1)	112.5 (13)	O(1)-N(1)-C(1)	108.8 (13)
Ni-N(2)-O(2)	127.1 (9)	Ni-N(2)-C(2)	115.6 (13)
O(2)-N(2)-C(2)	115.9 (13)	N(1)-C(1)-C(2)	112.4 (14)
N(1)-C(1)-N(3)	125.5 (17)	C(2)-C(1)-N(3)	122.1 (12)
N(2)-C(2)-C(1)	115.6 (14)	N(2)-C(2)-N(4)	124.9 (18)
C(1)-C(2)-N(4)	119.4 (15)	Ni-N(5)-O(3)	127.3 (9)
Ni-N(5)-C(3)	118.3 (10)	O(3)-N(5)-C(3)	110.6 (12)
Ni-N(6)-O(4)	127.8 (11)	Ni-N(6)-C(4)	119.0 (10)
O(4)-N(6)-C(4)	112.4 (13)	N(5)-C(3)-C(4)	111.1 (14)
N(5)-C(3)-N(7)	128.3 (14)	C(4)-C(3)-N(7)	120.4 (15)
N(6)-C(4)-C(3)	113.2 (14)	N(6)-C(4)-N(8)	122.1 (13)
C(3)-C(4)-N(8)	124.6 (15)	Ni-O(5)-C(5)	133.0 (11)
O(5)-C(5)-O(6)	124.4 (16)	O(5)-C(5)-C(6)	120.9 (15)
O(6)-C(5)-C(6)	114.7 (13)	C(5)-C(6)-C(7)	177.8 (17)
Ni-O(9)-C(9)	134.8 (10)	O(9)-C(9)-O(10)	128.2 (17)
O(9)-C(9)-C(10)	113.9 (14)	O(10)-C(9)-C(10)	117.8 (19)
C(9)-C(10)-C(11)	176.7 (20)		

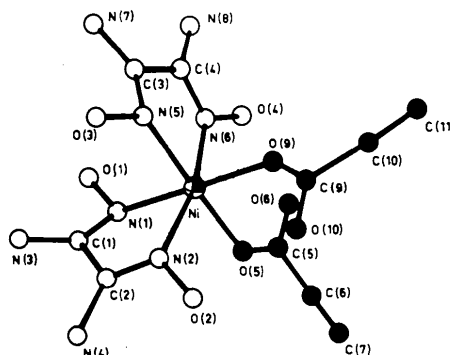


Fig. 1. The [Ni(C₃HO₂)(oaoH₂)] complex molecule showing the atom numbering. The thermal ellipsoid (50% probability) is drawn for Ni, other atoms as spheres with fixed radius 0.2 \AA . Filled spheres indicate the atoms of the propiolate ligands.

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A Heterometallic Biscarbyne Cluster,* $C_{27}H_{20}Co_2FeO_3$

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Abstract. $M_r = 566.17$, orthorhombic, $Pbca$, $a = 16.660$ (5), $b = 32.106$ (8), $c = 8.598$ (2) Å, $V = 4599$ Å³, $Z = 8$, $D_x = 1.63$ Mg m⁻³, $F(000) = 2288$, $\lambda(\text{Mo } K\alpha) = 0.70926$ Å, $\mu = 1.98$ mm⁻¹, $T = 293$ K. Refinement of 298 variables by full-matrix least-squares methods on F converged at agreement factors $R = 0.043$ and $R_w = 0.033$ using 2220 observations with $F^2 > 3\sigma(F^2)$. The triangular metal cluster formed by the $Fe(CO)_3$ and two $(\eta^5-C_5H_5)Co$ fragments is doubly capped by two $\mu_3\eta^1-C(C_6H_5)$ carbyne ligands derived from diphenylacetylene.

Introduction. As part of an investigation into the construction of heterometallic cluster compounds, we have explored the interchangeability of skeletal components such as $Co(CO)_3$, $(\eta^5-C_5H_5)Ni$ and diphenylacetylene (Freeland, Hux, Payne & Tyers, 1980). Similar approaches have been taken by Beurich & Vahrenkamp (1981), who prepared a heterometallic cluster monocapped with a $\equiv C-C_6H_5$ carbyne ligand, $[\mu_3\eta^1-C(C_6H_5)][(\eta^5-C_5H_5)Ni][Co(CO)_3]_2$, and by Fritch & Vollhardt (1980), who prepared the doubly capped $[\mu_3\eta^1-C(C_6H_5)]_2[(\eta^5-C_5H_5)Co]_3$ from diphenylacetylene and $(\eta^5-C_5H_5)Co(CO)_2$ in 72% yield. In each case the carbyne ligand(s) resulted from alkyne cleavage under the reaction conditions. We too have observed such alkyne cleavage in the formation of the title compound, which appeared as a minor product in all thermal reactions employed to prepare $[(\eta^5-C_5H_5)Ni][Fe(CO)_3][Co(CO)_3]C_2(C_6H_5)_2$ (Einstein, Freeland, Tyers, Sutton & Waterous, 1982). The dark-brown complex was separated by chromatography on Florisil, recrystallized from hexane, and mounted in a capillary under a N_2 atmosphere.

* 3,3,3-Tricarbonyl-1,2-bis(η^5 -cyclopentadienyl)-bis(μ_3 -phenylmethylidyne)-triangulo-dicobaltiron.

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Experimental. Space group $Pbca$, systematic absences k odd for $0kl$, l odd for $h0l$ and h odd for $hk0$. Crystal faces $\{100\}$, $\{010\}$, $\{121\}$, $\{1\bar{2}\bar{1}\}$, $\{1\bar{2}1\}$ and $\{1\bar{2}1\}$, approximate dimensions $0.41 \times 0.20 \times 0.03$ mm, $V = 0.0028$ mm³, $\{010\}$ faces well developed. Picker FACS-1 diffractometer, Vanderbilt operating system (Lenhart, 1975). Mo radiation, monochromatized by graphite, cell parameters from 25 reflexions $17^\circ < 2\theta < 28^\circ$, 4489 observations ($+h, +k, +l$) over 16 days by $\theta-2\theta$ scan, maximum 2θ 50° . 10 s stationary-crystal, stationary-counter background estimates, 1° , dispersion-corrected, scans for $2 \leq 2\theta \leq 35^\circ$; 20 s backgrounds for $2\theta > 35^\circ$. Standard reflections 200, 040, 200, 111, 102 and 104, average decay 12%, no correction applied. ω -scans (Furnas, 1957) had an average width at half-height of 0.11° before and after data collection. Background, monochromator polarization and Lorentz-polarization corrections applied and standard deviations assigned (Payne, 1973); $p = 0.03$ (Busing & Levy, 1957). Absorption correction by the analytical method [AGNOST (Cahen & Ibers, 1972)]; transmission factors from 0.646 to 0.936. 80 data with $k = \bar{1}$ also recorded; R factors for averaging were 0.021 and 0.020 before and after absorption correction. Solution by Patterson and Fourier techniques. Refinement by full-matrix least-squares methods, minimizing $\sum w(|F_o| - |F_c|)^2$, weight $w = 4F_o^2/\sigma^2(F_o^2)$. Neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965). Anomalous-dispersion contributions for Co and Fe (Cromer & Liberman, 1970). All 20 H atoms located and included in idealized positions (sp^2 hybridization, C–H 0.90 Å) with isotropic Debye factors 10% greater than those of bonded atoms. Convergence [298 variables and 2220 unique observations, $F_o^2 > 3\sigma(F_o^2)$] at $R = 0.043$ and $R_w = 0.033$, $S = 1.84$; $(\Delta/\sigma)_{\max} = 0.2$, final maximum $\Delta\rho$ excursion 0.4 (1) e Å⁻³ (at 0.441, 0.054, 0.163), of no chemical significance. Statistical analysis of R_w ,