

Table 3. *Relevant bond distances (Å) and angles (°); e.s.d.'s are given in parentheses*

Ru—C(1)	1.818 (12)	C(1)—O(1)	1.206 (14)
Ru—C(2)	1.913 (13)	C(2)—O(2)	1.139 (15)
Ru—C(3)	2.208 (13)	C(3)—C(4)	1.551 (16)
Ru—C(6)	2.299 (13)	C(4)—C(5)	1.532 (21)
Ru—C(7)	2.302 (13)	C(5)—C(6)	1.555 (20)
Ru—C(10)	2.204 (12)	C(6)—C(7)	1.395 (18)
Ru—P	2.313 (4)	C(7)—C(8)	1.495 (21)
Ru—M(1)	2.089	C(8)—C(9)	1.536 (22)
Ru—M(2)	2.192	C(9)—C(10)	1.538 (21)
		C(10)—C(3)	1.416 (16)
C(1)—Ru—C(2)	104.5 (5)	Ru—C(1)—O(1)	176 (1)
C(1)—Ru—P	90.5 (4)	Ru—C(2)—O(2)	179 (1)
C(2)—Ru—P	91.3 (4)	C(3)—C(4)—C(5)	113 (1)
M(1)—Ru—P	89.1	C(4)—C(5)—C(6)	113 (1)
M(2)—Ru—P	170.3	C(5)—C(6)—C(7)	123 (1)
M(1)—Ru—C(1)	138.4	C(6)—C(7)—C(8)	125 (1)
M(1)—Ru—C(2)	117.3	C(7)—C(8)—C(9)	114 (1)
M(2)—Ru—C(1)	91.2	C(8)—C(9)—C(10)	113 (1)
M(2)—Ru—C(2)	97.8	C(9)—C(10)—C(3)	123 (1)
M(1)—Ru—M(2)	83.3	C(10)—C(3)—C(4)	123 (1)

M(1) and M(2) are the mid-points of C(3)—C(10) and C(6)—C(7), respectively.

This is not so for Ru(CO)₂(η^4 -1,5-cyclooctadiene)-PPh₃, which is the object of the present structural analysis.

The coordination polyhedron about ruthenium is best described by the atoms C(1), C(2) and P, and the mid-points of the two C=C double bonds of the diene, which define a distorted trigonal bipyramid. The bidentate ligand occupies an axial and an equatorial site, the tertiary phosphine occupies an axial site. The C(3)—C(10) ring is practically in the equatorial plane (deviation 4°) and the two double bonds are almost parallel to each other. There is no obvious reason why the two CO bond lengths are significantly different. This is reflected in the observation of two IR bands [ν (CO) 1975 and 1920 cm⁻¹] for crystals ground in Nujol.

*d*⁸ metal diene complexes show a wide variety of fluxional behaviours on the IR time scale: Fe(CO)₃-(η^4 -1,3-diene) complexes are rigid, whereas the present complex exhibits two observable stereoisomers whose interconversion is slow, and Fe(CO)₃-(η^4 -1,5-cyclooctadiene) is stereochemically non-rigid on the IR time scale.

We thank the Swiss National Science Foundation for financial support.

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Acta Cryst. (1991). **C47**, 2664–2666

Structure of Pentaqua(glycine)nickel(II) Sulfate Monohydrate

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(Received 19 April 1991; accepted 5 June 1991)

Abstract. [Ni(C₂H₅NO₂)(H₂O)₅][SO₄·H₂O], *M*_r = 337.9, monoclinic, *P*2₁/*c*, *a* = 5.726 (1), *b* = 12.302 (2), *c* = 17.010 (2) Å, β = 97.92 (1)°, *V* = 1187 (1) Å³, *Z* = 4, *D*_m = 1.88 (2), *D*_x = 1.890 (1) Mg m⁻³, λ (Mo *K* α) = 0.71073 Å, μ = 1.83 mm⁻¹, *F*(000) = 704, *T* = 291 K, *R* = 0.026, 1938 unique observed reflections. The structure consists of [Ni(H₃⁺NCH₂COO⁻)(H₂O)₅]²⁺ cations, sulfate anions and water molecules. The coordination around Ni is distorted octahedral with bonds to one glycine O atom and five water molecules. This is probably the first case of monodentate oxygen coordination by the glycine zwitterion. The structure is stabilized by a system of hydrogen bonds involving

water–water, water–O(sulf.), water–O(Gly), O(sulf.)–N(Gly) and N(Gly)–O(Gly) interactions.

Experimental. The study of the title compound was undertaken as part of an investigation of nickel sulfate–glycine–water and nickel sulfate–triglycine sulfate–water systems, respectively. These systems are interesting within the bioinorganic chemistry framework and because of the possible formation of compounds with ferroelectric properties. The compound was prepared by evaporation of a dilute aqueous solution of glycine and nickel sulfate in 2:1 molar ratio. The crude green product was dissolved in water and the solution was allowed to stand in air for a few days. Green crystals obtained were stable in air and to X-rays. Density was determined by float-

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Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) of non-H atoms, with e.s.d.'s in parentheses

$$U_{\text{eq}} = [U_{22} + (U_{11} + U_{33} + 2U_{13}\cos\beta)/\sin^2\beta]/3.$$

	x	y	z	U_{eq}
Ni	986.3 (7)	2506.4 (5)	5534.6 (3)	16 (1)
N	3726 (4)	3813 (2)	3220 (1)	26 (1)
C1	1597 (5)	4400 (2)	3385 (1)	27 (1)
C2	575 (4)	3928 (2)	4087 (1)	21 (1)
O1	1831 (3)	3299 (1)	4539 (1)	26 (1)
O2	-1484 (3)	4242 (1)	4163 (1)	29 (1)
S	3620 (1)	648.9 (5)	3409.7 (3)	18 (1)
O3	1117 (3)	466 (1)	3482 (1)	28 (1)
O4	3786 (3)	1545 (1)	2840 (1)	29 (1)
O5	4639 (3)	-345 (1)	3120 (1)	35 (1)
O6	4894 (3)	943 (2)	4186 (1)	37 (1)
O7	-541 (3)	1258 (2)	4847 (1)	31 (1)
O8	412 (3)	1708 (1)	6546 (1)	23 (1)
O9	4182 (3)	1726 (1)	5594 (1)	22 (1)
O10	2777 (3)	3697 (1)	6219 (1)	25 (1)
O11	-2154 (3)	3325 (1)	5527 (1)	25 (1)
O12	-1574 (4)	2187 (2)	2650 (1)	46 (1)

Table 2. Selected interatomic distances (\AA) and angles ($^\circ$)

Ni...O1	2.068 (2)	C1—C2	1.515 (3)
Ni...O7	2.052 (2)	C2—O1	1.247 (3)
Ni...O8	2.047 (2)	C2—O2	1.264 (3)
Ni...O9	2.056 (2)	S—O3	1.473 (2)
Ni...O10	2.055 (2)	S—O4	1.479 (2)
Ni...O11	2.059 (2)	S—O5	1.463 (2)
N...C1	1.477 (3)	S—O6	1.463 (2)
		O12—O3	2.874 (3)
O1—Ni—O8	175.8 (1)	O3—S—O4	108.7 (1)
O7—Ni—O10	175.3 (1)	O3—S—O5	109.7 (1)
O9—Ni—O11	177.2 (1)	O3—S—O6	109.4 (1)
N—C1—C2	112.4 (2)	O4—S—O5	109.7 (1)
C1—C2—O1	118.1 (1)	O4—S—O6	109.7 (1)
C1—C2—O2	115.5 (2)	O5—S—O6	109.7 (1)
O1—C2—O2	126.3 (2)		

tion method (diiodomethane and tetrachloromethane). Crystal of size $0.2 \times 0.2 \times 0.5$ mm was used for the X-ray diffraction measurements on an Enraf-Nonius CAD-4-SPD73 diffractometer equipped with a graphite monochromator. Lattice parameters were determined by least squares from the setting angles of 21 reflections in the range $2.4 < \theta < 26^\circ$. Intensity data were collected with ω - 2θ scan, hkl range -7 to 6 , 0 to 15 , 0 to 20 , $2\theta < 52^\circ$. Two intensity reference reflections; loss in the intensity during the exposure time of 15 h was -0.8% . Absorption was ignored ($\mu R = 0.26$). 4851 reflections were measured of which 1938 unique observed reflections with $I > 1.96\sigma(I)$ were used ($R_{\text{int}} = 0.015$). Structure was solved by the heavy-atom method; the positions of Ni atoms were deduced from a vector map, the remaining non-H atoms were found from ρ maps and the H atoms from $\Delta\rho$ maps. Positional and anisotropic displacement parameters of non-H atoms and isotropic displacement parameters of H atoms were refined by the block-diagonal least-squares method minimizing $\sum w(|F_o| - |F_c|)^2$, $w = [\sigma^2(F_o) +$

$0.0009F_o^2]^{-1}$, to final $R = 0.026$ and $wR = 0.029$. 172 parameters were refined. Final $(\Delta/\sigma)_{\text{max}} = 0.041$ for U_{iso} of H8A; max. and min. heights of 0.30 and -0.56 e \AA^{-3} were present in the final $\Delta\rho$ map. Atomic scattering factors and corrections for anomalous dispersion were those from *International Tables for X-ray Crystallography* (1974). The calculations were performed on an ICL4-72 computer using programs *SHELXS86* (Sheldrick, 1990) and *SHELX76* (Sheldrick, 1976). The final atomic coordinates and equivalent isotropic temperature factors of non-H atoms are given in Table 1.* Selected interatomic distances and angles are given in Table 2. The formula unit is shown in Fig. 1. The thermal decomposition according to thermal analysis and differential thermal analysis in air begins at 356 K. No stepwise loss of the water was observed. The first step of the decomposition (complete dehydration and decomposition of glycine) is finished at 743 K, but the weight change does not correspond to the existence of any single entity. The second step of the decomposition begins at 883 K and is finished at 1223 K with NiO as the end product.

* Lists of H-atom parameters, bond distances and angles involving H atoms, anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54322 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

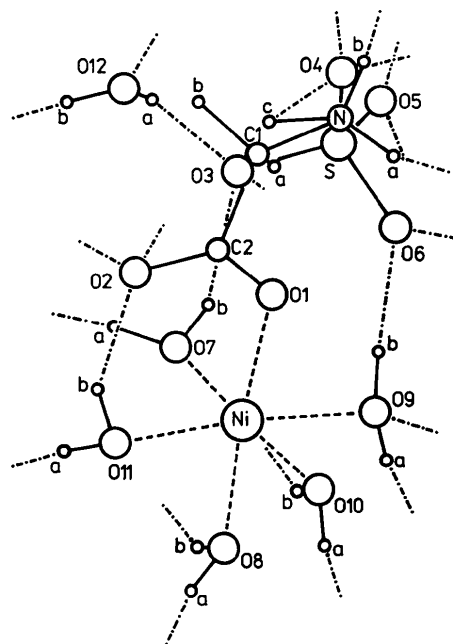


Fig. 1. A view of the formula unit along b with atom numbering. The coordination bonds are indicated by dashed lines, the hydrogen bonds by dashed and dotted lines.

Related literature. Two structures of the glycinate nickel compounds [diaquabis(glycinato-*O,N*)-nickel(II) (Castellano, Nascimento & Calvo, 1982); bis(glycinato-*N,O*)(2,2'-bipyridyl-*N,N'*)nickel(II) 5·5 hydrate (Žák, Głowiak, Kameníček & Březina, 1990)] are known. The coordination polyhedron around Ni can be approximated as an octahedron formed by the glycine O1 atom and by five water O atoms characterized by an average Ni—O distance of 2·056 (6) Å and O—Ni—O angle of 90 (2)° (with e.s.d.'s of arithmetic means in parentheses). This distance is significantly smaller than those in diaquabis(glycinato-*O,N*)nickel(II) [2·08 (1) Å; Castellano, Nascimento & Calvo, 1982], bis(glycinato-*N,O*)(2,2'-bipyridyl-*N,N'*)nickel(II) 5·5 hydrate [2·081 (2) Å; Žák, Głowiak, Kameníček & Březina, 1990] or in nickel oxide [2·084 (1) Å; Wyckoff, 1965]. Total bond valence of Ni—O calculated according to Brown & Altermatt (1985) equals 2·02 (theoretical value = 2·00). The glycine molecule is in its zwitterionic non-planar form: the N atom lies -0·335 Å out of the C1—C2—O1—O2 best plane located 0·002, -0·009, 0·003 and 0·003 Å from the defining atoms (see e.g. Solans, Franco & Miravittles, 1985). A comparison of this structure with glycine (Jönsson & Kvik, 1972) and triglycine sulfate (Solans, Franco & Miravittles, 1985; Žukov, Tafajenko & Fetisov, 1990) shows that the geometry of the amino acid is not significantly altered by coordination. The interplay among the distances and angles in the carboxylate group follows closely the relationships described by Borthwick (1980). Bond lengths and angles in the

sulfate anion are in the usual ranges. The O12 atom in the water molecule is 4·939 (2) Å from the Ni atom. The closest non-H atom of O12 is O8ⁱ ($i = \bar{x}, 0·5 + y, -0·5 - z$) located at a distance of 2·694 (2) Å. An inspection of the crystal packing shows that the bonding between the complex cation and the sulfate anion is predominantly ionic with the shortest distance O6—O9 = 2·664 (2) Å. All H atoms of water molecules and of the NH₃ group form hydrogen bonds with average distances and angles O^d—H^d = 0·87 (6), H^d...O^a = 1·9 (1), O^d...O^a = 2·76 (8) Å, O^d—H^d...O^a = 163 (7)° and N^d—H^d = 0·91 (2), H^d...O^a = 2·0 (1), N^d...O^a = 2·89 (10) Å and N^d—H^d...O^a = 166 (10)° (*d* indicates donor and *a* acceptor atoms).

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Acta Cryst. (1991). **C47**, 2666–2668

Semicarbazones and Thiosemicarbazones. XIV. Bis(2-methylthiosemicarbazide)-nickel(II) Nitrate

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(Received 17 September 1990; accepted 25 June 1991)

Abstract. C₄H₁₄N₆NiS₂·2NO₃, *M_r* = 393·0, triclinic, *P*1̄, *a* = 7·114 (3), *b* = 7·760 (2), *c* = 6·718 (3) Å, α = 93·10 (3), β = 101·60 (3), γ = 76·49 (3)°, *V* = 353·2 Å³, *Z* = 1, *D_x* = 1·85 g cm⁻³, λ(Mo *K*α) = 0·71073 Å, μ = 1·85 cm⁻¹, *F*(000) = 202, *T* = 293 K, final *R* = 0·046 for 1180 reflections with *F* > 3σ(*F*).

The Ni^{II} ion lies in a square-planar environment in a *trans* configuration. The ligands are coordinated as bidentate through the S and hydrazine N atoms. The influence of the methyl group on N(2) is mainly reflected in the Ni—S distance [2·177 (1) Å] which is longer, and the Ni—N and C—S bond lengths [1·894 (3) and 1·716 (4) Å, respectively], which are shorter than those reported for similar compounds.

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