

The Crystal and Molecular Structure of Bis(thioglycinato)nickel(II)

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The crystal structure of bis(thioglycinato)nickel(II), $\text{Ni}(\text{C}_2\text{H}_4\text{NOS})_2$, has been determined from nearly complete three-dimensional visually estimated X-ray diffraction data collected using $\text{Cu } K\alpha$ radiation, and refined by full-matrix least-squares methods to a final conventional R index of 0.139. The deep red-violet crystals have space group symmetry $P2_1/c$ with $a_0 = 7.231$, $b_0 = 10.784$, $c_0 = 11.100$ Å, $\beta = 105.7^\circ$, and with four molecules per unit cell. Two chemically similar, but crystallographically non-equivalent, molecules are found in the structure, each with a centrosymmetric square-planar arrangement of ligands about Ni(II). The geometries of these two molecules agree well. Each molecule participates in the maximum number of intermolecular hydrogen bonds. The bond lengths and angles agree well with those in similar compounds, except for the sulfur-carbon distances (1.721 ± 0.005 Å) which show appreciable multiple-bond character. Apart from the nitrogen and hydrogen atoms, each molecule is relatively planar.

Introduction

Bis(thioglycinato)nickel(II), $\text{Ni}(\text{SOCCH}_2\text{NH}_2)_2$, was synthesized (O'Halloran, 1968) in order to study the stereochemistry of coordination complexes of derivatives of 2-aminoethanethiol with transition metal ions. The diamagnetism of this complex and its electronic spectrum show that Ni(II) lies in a square-planar environment, but the low solubility of bis(thioglycinato)nickel(II) does not allow dipole moment measurements to be made to determine whether the coordinating ligands are arranged acentrically, as had been found in the structure of tetrakis-(2-aminoethanethiol)-trinickel(II) chloride (Wei & Dahl, 1970), or centrically as found in bis-(*N,N*-dimethyl-2-aminoethanethiol)-nickel(II) (Girling & Amma, 1967). In bis(glycinato)-nickel(II) dihydrate (Okaya, Pepinsky, Takeuchi, Kuroya, Shimada, Gallitelli, Stemple & Beevers, 1957) (Freeman & Guss, 1968), centric coordination is found.

The possibility of ligand-bridging in a multinuclear complex, as seen in the thiocarboxylate complex ethanolatotetra- μ -thiobenzoato-dinickel(II) (Bonamico, Dessy & Fares, 1969) (Melson, Greene & Bryan, 1970) and hexakis-(2-hydroxyethanethiolato)hexanickel(II) (Gould & Taylor, 1966), existed. It was not clear which two sites of the potentially tridentate ligand would coordinate.

Experimental

Crystals of bis(thioglycinato)nickel(II), supplied by J. W. Wrathall, H. J. O'Halloran, and R. L. Gavino, are long prismatic (a), deep violet in color, and predominantly twinned. The space group, $P2_1/c$, was assigned on the basis of Weissenberg photographs

($h0l$, $l = 2n$; $0k0$, $k = 2n$). Unit-cell dimensions at 25°C are: $a_0 = 7.231 \pm 0.002$, $b_0 = 10.784 \pm 0.001$, $c_0 = 11.100 \pm 0.002$ Å, and $\beta = 105.70 \pm 0.04^\circ$. The lengths of the reciprocal axes (but not β^*) were determined more accurately [$a^* = 0.14365$ (1), $b^* = 0.92726$ (5), and $c^* = 0.093579$ (5)] by a least-squares refinement of 398 2θ values measured on $hk0$ and $0kl$ Weissenberg photographs calibrated with reflections from a sample of 99.992% pure aluminum powder ($a_0 = 4.04961$ Å at 25°C). The measured density of 1.893 ± 0.002 g.cm $^{-3}$ agrees well with the value of 1.905 g.cm $^{-3}$ calculated for a four-molecule unit cell. The intensities of 1694 independent reflections (about 89% of the Cu sphere) were estimated visually from integrated Weissenberg films of the layers 0 to 6 along a and 0 to 10 along c ; the intensities of 1524 of these were above the minimum observable limit. $\text{Cu } K\alpha$ radiation ($\lambda = 1.5418$ Å), reasonably monochromated by means of a $K\beta$ (Ni) filter, was used throughout. Spherical absorption corrections ($\mu = 72.8$ cm $^{-1}$) were made, assuming an approximate crystal radius of 0.015 cm for the irregular crystal ($0.041 \times 0.046 \times 0.031$ cm) which was used throughout. The various layers of intensities were put onto a common scale using a least-squares program written by R. A. Sparks (Hamilton, Rollett & Sparks, 1965). At a late stage of refinement, 14 reflections (all those whose calculated structure factors exceeded 85 electron units and whose $\sin \theta/\lambda$ values were less than 0.3 Å $^{-1}$) were omitted because of apparent extinction.

Structure determination

The structure was solved both by direct methods (Karle, 1964), using a reiterative application (Long, 1965) of Sayre's equation, and by Patterson methods. The 200 values of E (the normalized structure factor) greater than 1.50 were used to generate 16 solutions. The most consistent solution, for which convergence

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Table 1. Observed and calculated structure factors

The running index is h; values for k and l for each group immediately precede that group. The central column is 10|F_o|. The right-hand column is 10F_c. The F_o listed for unobserved reflections is 1/3 F_min. The symbols immediately following some values of F_o have these meanings: U, unobserved; E, suffers from apparent extinction and is excluded from least-squares refinement.

Table with multiple columns containing numerical data for structure factors, including observed (F_o) and calculated (F_c) values, and various symbols (U, E) indicating observation status.

was the most rapid, was essentially correct, although it showed little detail and seemed wrong initially. All but 13 of the phases were positive. The Patterson synthesis offered three solutions, two of which coincided with the results of direct methods. One of these two sets of Ni and S positions revealed the remaining nonhydrogen atoms in one step of Fourier refinement. Full-matrix least-squares refinement, including only observed reflections and omitting reflections suffering from apparent extinction, with anisotropic temperature factors for the nonhydrogen atoms, eventually brought the unweighted R index for observed reflections to 0.139, where $R = \sum(|F_o| - |F_c|) / \sum|F_o|$.

The final difference map, with its standard deviation of $0.5 \text{ e.}\text{\AA}^{-3}$, did not reveal the hydrogen positions, so these were calculated assuming that the atoms to which hydrogen was bonded were tetrahedrally coordinated, the C-H bond length was 1.08 \AA , and the N-H bond length was 1.01 \AA . Each hydrogen atom was assigned an isotropic temperature factor equal to that of the atom to which it was bonded. The program used (UCLALS 4) was that of Gantzel, Sparks & Trueblood [American Crystallographic Association Program Library (old) No. 317, modified] which minimizes $\sum w(\Delta|F|)^2$. Hughes (1941) weights, modified to account for the number of times a reflection was observed, were used. The intensities of about 93% of the unobserved reflections were calculated to be less than the minimum observable intensity (I_{\min}), and none was as great as $1.2 I_{\min}$.

The scattering factors used were: O, N, and C (valence) (Hoerni & Ibers, 1954), H (bonded) (Stewart, Davidson & Simpson, 1965), $S^{-1/2}$ (Dawson, 1960) and Ni^{+1} (Watson & Freeman, 1961). The latter two scattering factors were modified for the real part of the anomalous dispersion correction (Dauben & Templeton, 1955). In the last cycle of least-squares refinement,

all shifts were less than 0.01 estimated standard deviations of position. Observed and calculated structure factors are listed in Table 1. The final positional and thermal parameters are given in Tables 2 and 3 respectively.

Table 2. Final positional parameters and their standard deviations

Values are given $\times 10^4$. See Fig. 1 for the identities of the atoms. E.s.d.'s are in the units of the least significant digit given for the corresponding parameter.

	x	y	z
Ni(1)	0	0	0
S(2)	337 (2)	1130 (1)	-1562 (1)
C(3)	-218 (9)	2569 (6)	-1100 (6)
O(4)	-294 (9)	3531 (5)	-1723 (5)
C(5)	-627 (11)	2641 (6)	163 (6)
N(6)	-1209 (7)	1409 (5)	552 (5)
Ni(7)	5000	0	5000
S(8)	5291 (2)	-1667 (1)	3938 (1)
C(9)	4826 (9)	-1044 (5)	2457 (6)
O(10)	4744 (7)	-1651 (4)	1506 (5)
C(11)	4552 (10)	338 (5)	2369 (6)
N(12)	3910 (8)	817 (4)	3437 (5)
H(5A)	654	2950	851
H(5B)	-1771	3302	114
H(6A)	-923	1337	1487
H(6B)	-2646	1375	210
H(11A)	5890	781	2371
H(11B)	3480	562	1506
H(12A)	4199	1732	3583
H(12B)	2469	747	3273

Crystal and molecular structure

Two chemically similar centric bis(thioglycinato)-nickel(II) molecules (I and II, Fig. 1) are found at two nonequivalent inversion centers [Wyckoff positions $2(a)$ and $2(d)$] of $P2_1/c$. Each molecule can be discussed in terms of three least-squares planes as presented in

Table 3. Thermal parameters and their standard deviations

The b 's are $\times 10^4$. See Fig. 1 for the identities of the atoms. E.s.d.'s are in the units of the least significant digit given for the corresponding parameter.

I. Nonhydrogen temperature factor = $\exp[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
Ni(1)	144 (4)	63 (2)	29 (2)	25 (3)	43 (4)	17 (2)
S(2)	208 (4)	72 (1)	44 (2)	31 (3)	102 (4)	22 (2)
C(3)	148 (13)	76 (5)	36 (5)	-31 (13)	30 (13)	15 (8)
O(4)	310 (15)	69 (4)	53 (5)	-40 (12)	65 (14)	8 (7)
C(5)	242 (18)	65 (5)	45 (6)	-47 (14)	68 (16)	-8 (8)
N(6)	167 (12)	55 (4)	40 (5)	10 (10)	46 (12)	17 (6)
Ni(7)	149 (4)	34 (1)	40 (2)	-2 (2)	18 (4)	-5 (2)
S(8)	214 (4)	38 (1)	45 (2)	23 (3)	33 (4)	-4 (2)
C(9)	165 (14)	37 (4)	49 (6)	1 (10)	23 (13)	-14 (7)
O(10)	201 (11)	60 (4)	51 (4)	27 (10)	18 (11)	-25 (6)
C(11)	213 (16)	38 (5)	58 (6)	-11 (12)	64 (16)	8 (8)
N(12)	209 (13)	36 (4)	39 (4)	13 (10)	29 (11)	-5 (6)

II. Hydrogen

H(5A)	2.23 \AA^2	H(11A)	3.22 \AA^2
H(5B)	2.23	H(11B)	3.22
H(6A)	2.43	H(12A)	2.21
H(6B)	2.43	H(12B)	2.21

Table 4. The first is exactly planar by symmetry; the second is very nearly so since it contains a trigonal carbon atom; the last shows that, apart from the nitrogen and hydrogen atoms, each molecule is itself approximately planar. The deviations of the atoms from these planes are given in Table 4.

Corrections to the observed bond lengths due to the foreshortening effect of riding motion (Busing & Levy, 1964) were calculated but were not applied. All correc-

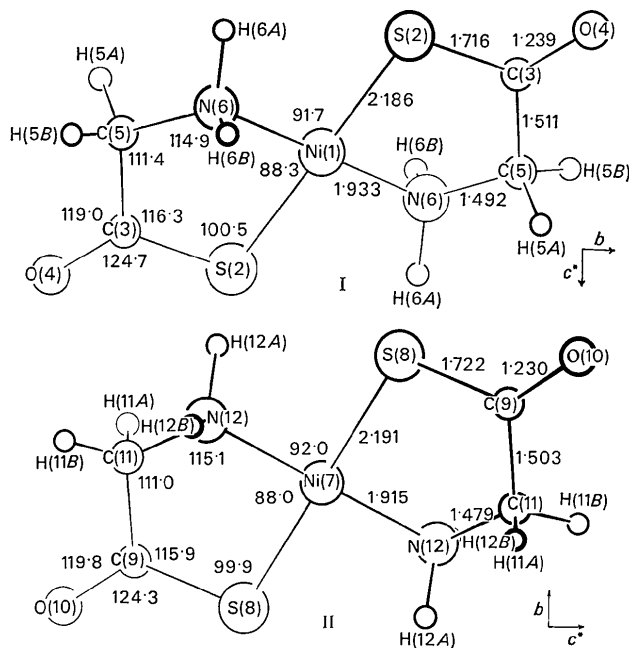


Fig. 1. Bis(thioglycinato)nickel(II), molecules I and II. The e.s.d.'s are as follows: Ni-S, 0.002 Å; Ni-N, 0.005 Å; S-C, 0.007 Å; C-C, C-O, C-N, 0.008 Å; angles at Ni, 0.2°; other angles, 0.3 to 0.6°.

tions were less than one standard deviation of the corresponding bond length, except those for C(3)-O(4) and C(9)-O(10) which were 0.009 and 0.014 Å respectively. All chemically equivalent bond lengths in molecules I and II are in good agreement except those involving nickel, and these do not differ significantly. The bond angles in molecules I and II all agree well. Fig. 2 shows that each molecule participates in the maximum number of hydrogen bonds: each oxygen atom is approached by two amino hydrogen atoms in neighboring molecules, and each amino hydrogen atom approaches an extramolecular oxygen atom. The twist of the amino groups from the general molecular planes of molecules I and II (see Table 4) effectively makes all N-H bonds axial or equatorial with respect to these planes.

The angles around the nickel(II) ions differ significantly from 90°, but they agree well with those found in bis-(*N,N*-dimethyl-2-aminoethanethiol)nickel(II) (Girling & Amma, 1967). There, the Ni-N distance is 0.04 Å longer than that found in this work, presumably due to the effect of the amino methyl groups (Girling & Amma, 1967). Altogether, the Ni-S, C-N, and C-C bond lengths found lie in the range of those given in a recent tabulation (Wei & Dahl, 1970) of bond lengths found in square-planar Ni(II) complexes of 2-amino-ethanethiol and its derivatives. The Ni-N distance is 0.02 Å longer in bis(thioglycinato)nickel(II) than that given in the above tabulation, but the S-C distance is 0.11 Å shorter, indicating that the S-C bond has appreciable multiple-bond character. The average distance here, 1.719 ± 0.005 Å, agrees well with the 'double bond' length (1.71 ± 0.02 Å) found in *N,N'*-ethylenethiourea (Wheatley, 1953) and the 'double bond' lengths found in bis(thiourea)copper(I) chloride (Spofford & Amma, 1970) but it is appreciably longer than the bond in CS₂ (1.55 Å) (Guenther, 1959) and

Table 4. Deviations of atoms from least-squares planes (Å × 10³)

Boldface deviations indicate the atoms used to define the least-squares plane. A negative deviation from a plane indicates that the atom with the coordinates given in Table 2 lies between that plane and the origin. Primed atoms are related to those given in Table 2 by inversion through the corresponding Ni. The direction cosines (× 10⁴), *q*, are with respect to *a*, *b*, *c**. The r.m.s. deviation (Å × 10³) of the boldface atoms from the plane is δ . *D* is the distance (in Å) from the plane to the origin.

	Plane No.			Plane No.		
	1	3	5	2	4	6
Ni(1)	0	-110	0	Ni(7)	0	-146
S(2)	0	0	5	S(8)	0	7
C(3)	342	-2	-1	C(9)	344	-7
O(4)	397	1	-50	O(10)	391	2
C(5)	597	1	66	C(11)	625	3
N(6)	0	-518	-399	N(12)	0	-558
S(2')	0		-5	S(8')	0	-7
C(3')	-342		1	C(9')	-344	2
O(4')	-397		50	O(10')	-391	58
C(5')	-597		-66	C(11')	-625	-95
N(6')	0		399	N(12')	0	398
<i>q_a</i>	7702	8846	8675		9545	9836
<i>q_b</i>	3115	1685	1471		2971	1284
<i>q_c*</i>	5565	4348	4751		-254	1269
<i>D</i>	0	0.110	0		1.882	2.902
δ	0	1	39		0	4
						53

longer than the sum of the Pauling double-bonded covalent radii (Pauling, 1960), 1.61 Å. The Ni(II)–S–C angle ($99.9 \pm 0.2^\circ$) agrees with the corresponding angle in bis-(*N,N*-dimethyl-2-aminoethanethiol)nickel(II) ($100.8 \pm 0.5^\circ$) (Girling & Amma, 1967). The average C–O bond length (including the riding correction) of 1.246 ± 0.006 Å in bis(thioglycinato)nickel(II) is insignificantly longer than the accepted 'doubly bonded' value of 1.23 ± 0.01 Å (Sutton, 1965). It is much longer here, however, than the double bond in CO₂ (1.16 Å) (Courtoy, 1959). There is, then appreciable π -conjugation in the thiocarboxylate group, as is found in ethanolatotetra-(μ -thiobenzoato)dinickel(II) (Bonamico, Dessy & Fares, 1969; Melson, Greene & Bryan, 1970). Dihedral angles are listed in Table 5, and some nonbonded interatomic distances are given in Table 6.

Table 5. Dihedral angles

Ni(1)–S(2)–C(3)–C(5)	3.1°
Ni(7)–S(8)–C(9)–C(11)	4.5
S(2)–C(3)–C(5)–N(6)	22.1
S(8)–C(9)–C(11)–N(12)	24.6
C(3)–C(5)–N(6)–Ni(1)	33.3
C(9)–C(11)–N(12)–Ni(7)	36.2

Table 6. Some nonbonded interatomic distances*

(<i>x</i> , <i>y</i> , <i>z</i>)†	Ni(1)·····H(11 <i>B</i>)	2.69 Å
(– <i>x</i> , – <i>y</i> , – <i>z</i>)	S(2)·····H(12 <i>B</i>)	3.1
	C(3)·····O(10)	3.33
	C(5)·····O(10)	3.23
	H(5 <i>B</i>)·····O(10)	3.0
	H(6 <i>B</i>)·····C(9)	3.0
(– <i>x</i> , $\frac{1}{2}+y$, $\frac{1}{2}-z$)	H(5 <i>B</i>)·····Ni(7)	3.0
	H(5 <i>B</i>)·····S(8)	3.0
(<i>x</i> , $\frac{1}{2}-y$, $\frac{1}{2}+z$)	H(6 <i>A</i>)·····C(3)	2.8
	H(12 <i>B</i>)·····C(3)	2.9
(– <i>x</i> , $-\frac{1}{2}+y$, $-\frac{1}{2}-z$)	S(2)·····O(4)	3.38
(<i>x</i> , $-\frac{1}{2}-y$, $-\frac{1}{2}+z$)	O(10)·····S(8)	3.49
(1– <i>x</i> , $-\frac{1}{2}+y$, $\frac{1}{2}-z$)	S(8)·····H(5 <i>A</i>)	2.9
	O(10)·····C(11)	3.47
	C(9)·····H(12 <i>A</i>)	2.8
(1+ <i>x</i> , $\frac{1}{2}-y$, $\frac{1}{2}+z$)	H(11 <i>A</i>)·····O(4)	2.8

* All intermolecular distances less than the following are given: H...H, 2.7 Å; H...non-H, 3.1 Å; non-H...non-H, 3.5 Å. Hydrogen bonds are shown in Fig. 2, and are omitted here.

† The first atom of each pair has coordinates as given in Table 2. The second atom is related to the first by the symmetry operation given in the subheading.

Thermal motion

The motions of several different centrosymmetric groups of atoms have been analyzed in terms of the rigid-body tensors of translation (**T**) and libration (**L**) (Schomaker & Trueblood, 1968) using program *TLS6* [Schomaker & Trueblood, *ACA* (new) No. 1]. The

root-mean-square discrepancy between observed and calculated U_{ij} , as well as the standard deviations of **L** components, serves as a measure of the applicability of the analysis and, thus, of the rigidity of a particular grouping. Analyses were performed for groupings of composition NiS₂O₂N₂C₄, NiS₂N₂C₄, and NiS₂N₂ for each molecule. Molecule I exhibits r.m.s. U_{ij} values of 0.0044, 0.0038, and 0.0019 Å², while the corresponding values for molecule II are 0.0021, 0.0019, and 0.0008 Å². Molecule II, at least, is surprisingly rigid. The results for the two largest groupings are the most reliable, and these are presented in Table 7. In both cases the principal librations of 5.7 and 5.3° are about axes nearly normal to **a** and can, accordingly, be readily located in Fig. 1. Thermal ellipsoids of 90% probability for molecules I and II are shown in Fig. 3.

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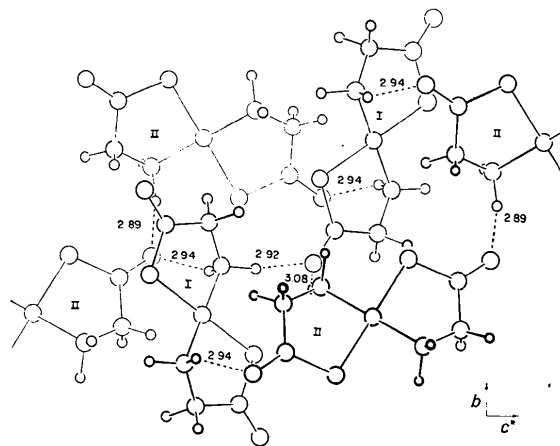


Fig. 2. The packing and hydrogen bonding of molecules I and II in the bis(thioglycinato)nickel(II) crystal structure.

Table 7. *Rigid-body thermal parameters*

The axes of reference are a , b , and c^* . The e.s.d.'s of the components of L are given after them in the units of the least significant figure.

$L[\times 10^{-1}(\text{°})^2]$	Bis(thioglycinato)nickel(II) molecule I (all nonH atoms)			Bis(thioglycinato)nickel(II) molecule II (all nonH atoms)		
		23 (9)	-32 (17)	8 (11)	27 (6)	-17 (6)
		291 (67)	-76 (22)		42 (8)	69 (9)
			105 (16)			259 (30)

Principal axes of L

	R.m.s. amplitude	Direction cosines ($\times 10^3$)			R.m.s. amplitude	Direction cosines ($\times 10^3$)		
		$L1$	5.7	110		-937	333	5.3
$L2$	2.8	-041	330	943	1.9	759	-611	226
$L3$	1.4	993	117	-001	1.0	649	740	-178

Principal axes of reduced $* T$

	R.m.s. amplitude	Direction cosines ($\times 10^3$)			R.m.s. amplitude	Direction cosines ($\times 10^3$)		
		$(\overline{\Delta U_{ij}^2})^{1/2}(\text{Å}^2)$	0.20 Å	-408		912	026	0.20 Å
	0.16	912	406	061	0.16	088	-127	988
	0.13	045	049	-998	0.13	123	986	116
		0.0044				0.0021		

* Corresponding to equation (20) of Schomaker & Trueblood (1968).

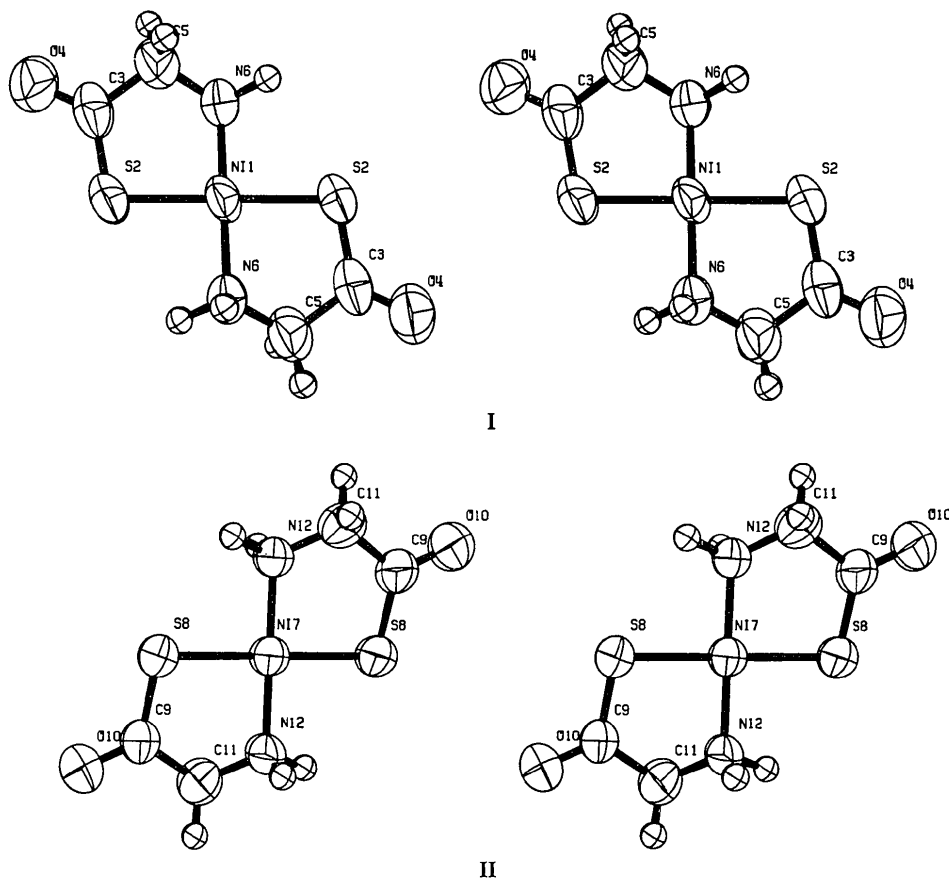


Fig. 3. Stereoviews of molecules I and II of bis(thioglycinato)nickel(II), showing ellipsoids of 90% probability.

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Structures Cristallines de l'Oxo-diperoxo-hexaméthylphosphoramido-aquo-molybdate(VI) et de l'Oxo-diperoxo-hexaméthylphosphoramido-pyridino-molybdate(VI)

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The crystal structures of $\text{MoO}(\text{O}_2)_2\text{PO}[\text{N}(\text{CH}_3)_2]_3\text{H}_2\text{O}$ (*A*) and $\text{MoO}(\text{O}_2)_2\text{PO}[\text{N}(\text{CH}_3)_2]_3\text{C}_5\text{H}_5\text{N}$ (*B*) have been determined. Three-dimensional X-ray data were collected on a linear diffractometer ($\text{Mo K}\alpha$ radiation). The structures were solved by Patterson methods and refined by full-matrix least-squares analysis to a reliability index $R=0.032$ for (*A*) and $R=0.048$ for (*B*). In each compound the molybdenum atoms are surrounded by seven atoms forming a pentagonal bipyramid. The equatorial plane of the bipyramid contains the two peroxy groups and the oxygen atom of the phosphoramido. The apical positions are occupied by a double-bonded oxygen atom and a water molecule for (*A*) and a pyridine molecule for (*B*).

Introduction

Les deux composés $\text{MoO}_5(\text{HMPT})(\text{H}_2\text{O})$ (*A*) et $\text{MoO}_5(\text{HMPT})(\text{Py})$ (*B*), qui font l'objet de la présente étude, font partie d'une classe de composés peroxydés du molybdène(VI) dont l'existence a été signalée récemment (Mimoun, Sérée de Roch & Sajus, 1969).

La molécule d'eau présente dans le composé (*A*) est très mobile. Ce composé donne lieu à de multiples réactions d'échange, en particulier avec la pyridine pour donner le composé (*B*). Sa déshydratation est aisée, elle fournit $\text{MoO}_5(\text{HMPT})$ qui réagit sélectivement avec les hydrocarbures oléfiniques pour donner des époxydes avec un rendement élevé (Mimoun, Sérée de Roch & Sajus, 1970).

Partie expérimentale

Préparation et recristallisation

Les deux composés (*A*) et (*B*) ont été préparés conformément à la méthode décrite par Mimoun, Sérée de

Roch & Sajus (1969). Les monocristaux nécessaires à notre étude ont été obtenus par recristallisation dans l'éthanol pour le composé (*A*) et dans le dichloroéthane pour le composé (*B*). A température ordinaire, ces deux peroxydes se décomposent lentement, ils peuvent être conservés pendant plusieurs semaines à l'abri de la lumière vers 0°C .

Données cristallographiques et enregistrement des intensités

Les dimensions de la maille élémentaire et le groupe spatial de chaque composé ont été déterminés sur chambre de précession étalonnée, à la longueur d'onde $\text{K}\alpha$ du molybdène. Les densités ont été mesurées par picnométrie dans le xylène.

Composé (*A*): $\text{MoO}_5(\text{HMPT})(\text{H}_2\text{O})$ cristallise dans le système monoclinique avec le groupe spatial $P2_1/c$ (no. 14). Les paramètres de la maille cristalline ont les valeurs suivantes.

$$\begin{array}{ll} a = 10,648 \pm 0,009 \text{ \AA} & V = 1478 \text{ \AA}^3 \\ b = 8,299 \pm 0,007 & M = 373 \\ c = 17,288 \pm 0,015 & Z = 4 \\ \beta = 104,70 \pm 0,15^\circ & \end{array}$$

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