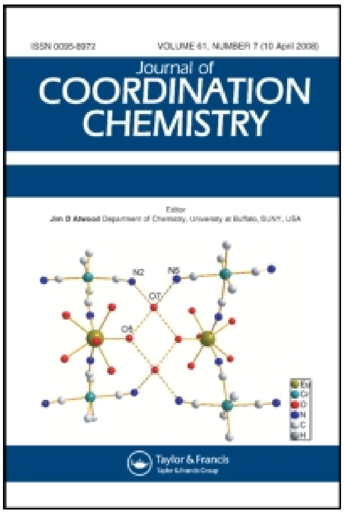

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Synthesis, characterization and crystal structure of a novel Ni(II) complex, $Ni(L-H)_2$ (L = 3,5-dimethyl-1-thiocarboxamidopyrazole)

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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF A NOVEL Ni(II) COMPLEX, $Ni(L\text{-}H)_2$ (L = 3,5-DIMETHYL-1-THIOCARBOXAMIDOPYRAZOLE)

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A new complex, $Ni(L\text{-}H)_2$, L = 3,5-dimethyl-1-thiocarboxamidopyrazole, has been synthesized and characterized by IR spectroscopy, magnetic and electrical measurements. Its crystal structure was solved from powder X-ray diffraction data. The compound crystallizes in space group $P\bar{1}$ with two independent half-molecules containing Ni(II) coordinated by four nitrogen atoms in a square-plane. The packing pattern consists of two stacks of parallel molecules mutually tilted at an angle of 118°.

Keywords: Ni(II) complexes; Pyrazole-based ligands; Powder diffraction; Structure

INTRODUCTION

Metal complexes containing pyrazole ligands have attracted considerable interest owing to the interesting coordination chemistry of these phases and their biological and biochemical importance [1–4]. Pyrazole ligands are interesting from the standpoint of drug design; they find applications in antipyretics and antirheumatics, and also in herbicides and fungicides [5,6]. Some pyrazole derivatives are used as metal ion extragents [3]. In recent years, new developments have been made in the biocoordination chemistry of pyrazole and its derivatives [7–11]. They include new macrocyclic pyrazole-based ligands important in oxygen-transfer biochemistry [12] and formation

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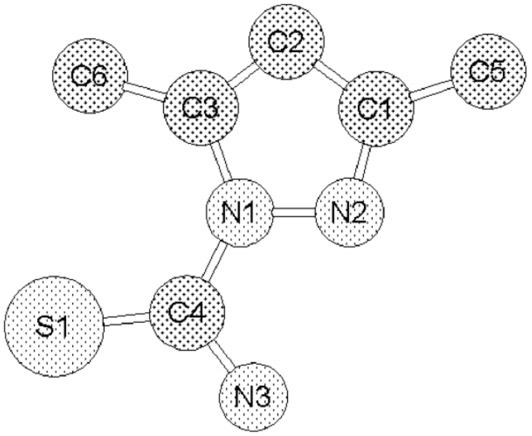

FIGURE 1 Ligand L.

of three-dimensional structures around the active sites of copper proteins [13–15]. We have synthesized and characterized a number of pyrazole-based ligands and their metal complexes [16–20]. The aim of these studies is to investigate the influence of pyrazole ring substituents on complex formation. Recently we reported the crystal structure of 3,5-dimethyl-1-thiocarboxamidopyrazole [21], (Fig. 1) as well as its Co(III) complex, Co(L-H)$_3$ [22].

Recently, powder diffraction methods have proved to be powerful tools for structural characterization of materials. Particular advances have been made in the area of direct space approaches, where the correctness of trial structures generated independently of the observed diffraction data is evaluated using appropriate agreement factors based on the comparison between calculated and experimental powder patterns. Methods including simulated annealing, Monte Carlo and genetic algorithm techniques have been applied successfully to structure solution of molecular solids [23]. For this type of structure, complexity is imparted by the number of degrees of freedom, namely the number of torsion angles in a molecule and the number of crystallographically independent molecules.

In this article we report the synthesis of the complex Ni(L-H)$_2$, L = 3,5-dimethyl-1-thiocarboxamidopyrazole, its characterization and structure solution from powder X-ray diffraction data.

EXPERIMENTAL

Synthesis

The complex was synthesized by mixing a cold methanolic solution of the ligand (2.5 mmol) and $NiSO_4 \cdot 7H_2O$, $Ni(OAc)_2$, $Ni(CF_3COO)_2$ or $Ni(SCN)_2$ (1 mmol). The total volume of the solution after mixing was about 10 cm^3. After the mixture was allowed to stand for four hours, the product was filtered off, washed with methanol and water and dried at room temperature. The final product is scarlet and consists of acicular microcrystals. The same product is obtained with any of the Ni(II) salts listed.

Physical Measurements

Carbon, hydrogen and nitrogen contents were determined by standard analytical methods. Ni(II) was determined by titration with EDTA. Elemental analysis: found (calcd.) (%): C 39.06 (39.26), H 4.40 (4.39), N 22.20 (22.89) and Ni 15.32 (15.92). Infrared spectra were recorded on a Perkin-Elmer 1760X FTIR spectrophotometer. IR spectrum (cm^{-1}, KBr): 3422b, 3079b, 1564s, 835m, 766w, 679s, 638s, 501s, 420m. The molar conductivity of a freshly prepared $10^{-3}\,mol\,dm^{-3}$ solution of the compound in DMF was measured at room temperature using a Jenway 4010 digital conductivity meter. The conductivity is low ($6.11\,S\,cm^2\,mol^{-1}$), indicating the non-electrolyte character of the complex in this solvent. The magnetic moment of the complex was measured using a Sherwood Scientific Ltd, Cambridge MSB-MKI magnetic susceptibility balance. Data were corrected for diamagnetic susceptibility. The complex is diamagmetic, thus suggesting, together with its colour, square planar coordination for Ni(II).

X-ray Diffraction Data Collection

Powder X-ray diffraction data were collected using a Bruker AXS D8 Advance diffractometer equipped with an mBraun linear PSD and a Ge(111) incident beam monochromator. A small amount of sample was loaded in a glass capillary of diameter 0.5 mm to a depth of about 4 cm and sealed. The capillary was kept spinning during data collection. Two consecutive powder patterns were collected in the 2θ range 5 to 60° in 0.0144° steps, each with a count time of 0.5 s per step and summed to produce the final data set.

Analysis

The powder pattern was indexed using an in-house modification of the program of Visser [24]. Positions of 27 reflections were accurately determined by peak fitting and were assigned confidence labels. An iterative procedure was set up where a subset of 20 reflections was selected for each run of autoindexing. This routine gave the best figure of merit of $M_{20} = 32$ for a triclinic unit cell with parameters $a = 11.189$, $b = 15.315$, $c = 4.467$ Å, $\alpha = 87.5$, $\beta = 86.1$ and $\gamma = 89.0°$, which accounted for all observed reflections. The volume of about 763 Å^3 corresponds to two molecules of $Ni(L\text{-}H)_2$ in the unit cell. A Pawley fit [25] carried out in space group $P\bar{1}$ gave good agreement with the data. In order to create an internal coordinate representation of the molecule to be used for the structure solution, all possible conformations of $Ni(L\text{-}H)_2$ were considered and four models constructed using standard bond lengths and angles (Fig. 2): (a) N_4 *trans*-metal–ligand bonding through four N atoms in a *trans* conformation; (b) N_4 *cis*-metal–ligand bonding through four N atoms in a *cis* conformation; (c) N_2S_2 *trans*-metal–ligand bonding through two N and two S atoms in a *trans* conformation; (d) N_2S_2 *cis*-metal–ligand bonding through two N and two S atoms in a *cis* conformation.

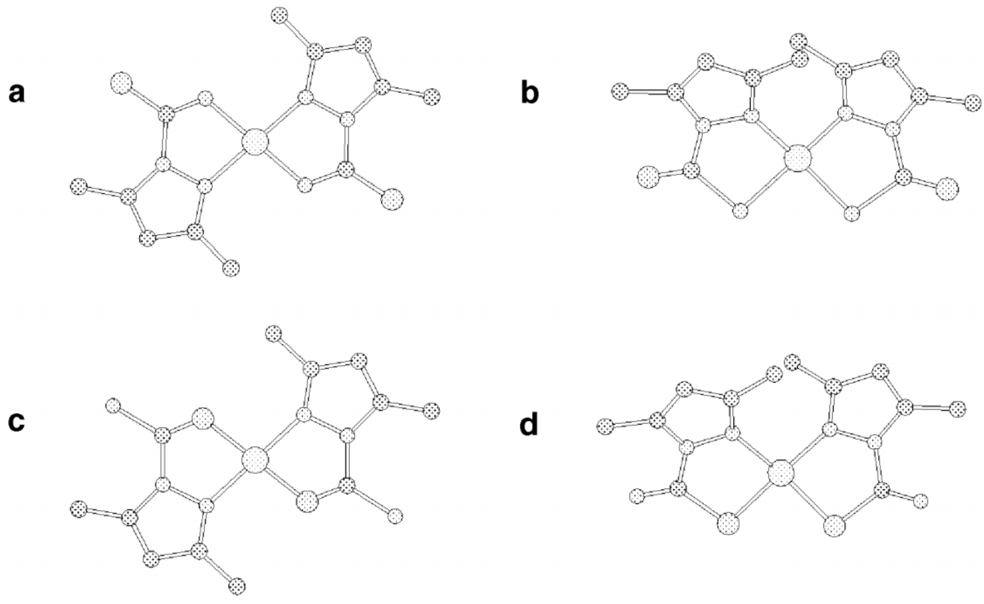

FIGURE 2 Four molecular models used for trial structure solution of Ni(L-H)$_2$.

TABLE I Agreement factors, χ^2, obtained from trial structure solution using eight different models

	$P1$	$P\bar{1}$
N$_4$ *trans*	12.23	39.20
N$_4$ *cis*	73.34	43.15
N$_2$S$_2$ *trans*	45.74	39.25
N$_2$S$_2$ *cis*	78.41	49.91

Structure solution was carried out using a simulated annealing approach implemented in the program DASH [26]. The molecule was treated as a rigid unit and the only parameters adjusted were the six external degrees of freedom, three translations and three molecular rotations. For each of the possible models, 10 runs of a maximum of 1×10^7 annealing moves were performed, starting with an annealing temperature of 1000 K and a cooling rate of 0.02 K. However, attempts to solve the structure in space group $P\bar{1}$ using a whole molecule in any of the four conformations as the asymmetric unit were not successful. The same procedure was then performed in the non-centrosymmetric space group $P1$, using two independent Ni(L-H)$_2$ molecules with a total of 42 non-hydrogen atoms as an asymmetric unit. This increased the number of adjustable parameters to twelve. A summary of the agreement factors, χ^2, for all simulated annealing runs is given in Table I. It is immediately apparent that the model with the ligands bond *trans* to the metal through the nitrogen atoms of the pyrazole rings and the thiocarboxamide groups gives by far the best agreement with the observed data. The best solution had a χ^2 value of 12.23 and was found after 1 365 000 moves. The same solution was found in nine out of ten simulated annealing

TABLE II Crystallographic and structure refinement details

Formula	$NiC_{12}H_{16}N_6S_2$
Wavelength (Å)	1.5406
Data range used 2θ (°)	5–60
Step size (°)	0.0144
Space group	$P\bar{1}$
a (Å)	11.189(1)
b (Å)	15.321(2)
c (Å)	4.4673(3)
α (°)	87.532(6)
β (°)	86.121(5)
γ (°)	88.968(6)
V (Å^3)	763.3 (2)
Z	2
Number of profile points	3869
Number of soft restraints	46
Total number of observations	3915
Number of parameters refined	84
R_p (%)	4.60
wR_p (%)	6.32
R_F^2 (%)	13.10

runs. The atomic coordinates from this solution were used as a starting model for structure refinement.

Rietveld refinement [27] was carried out within the GSAS software suite [28]. In the initial cycles, all structural parameters except for unit cell constants were kept fixed, and the additional variables refined were 12 terms of a Chebyshev polynomial describing the background, 3 profile terms, the zero point and the scale factor. Following convergence of these parameters, a number of restraints were introduced in order to perform a full Rietveld refinement, i.e., refine the positions of all 42 non-hydrogen atoms in addition to the general parameters mentioned above. Eight planar restraints were set up, four governing the relative positions of the seven atoms of the substituted pyrazole ring [atoms N(1), N(2), C(1), C(2), C(3), C(5) and C(6) in Fig. 1, and three more analogous rings in the asymmetric unit] and four governing the relative positions of the thiocarboxamide group [N(1), N(3), C(4) and S(1), and the remaining three analogous groups in the asymmetric unit]. In order to determine appropriate values for bond length restraints for the non-hydrogen atoms, seven Cambridge Structural Database [29] searches were carried out. For each type of bond length, the ideal value taken as the mean of its distribution in the CSD was used to define the restraint. Hydrogen atoms were placed geometrically. This gave a total of 80 bond length restraints. Rietveld refinement was then performed in which the coordinates of all non-hydrogen atoms and an overall isotropic temperature factor were varied and this gave an excellent fit to the data. However, inspection of the model obtained revealed that the true arrangement of molecules in this crystal structure was centrosymmetric and a new asymmetric unit was constructed in space group $P\bar{1}$ [30]. This model was used for a restrained Rietveld refinement with the protocol described above and the final agreement factors obtained were $R_p = 4.60\%$, $wR_p = 6.32\%$ and $R_F^2 = 13.10\%$. Details of the refinement are given in Table II. Full lists of crystallographic data are available from the authors upon request.

DISCUSSION

The crystal structure of the title compound consists of discrete neutral molecules of formula [Ni(L-H)$_2$]. The ligands are *trans*-coordinated to the central Ni(II) ion through the nitrogen atoms of the pyrazole ring and the thiocarboxamide group. Thiocarboxamide ligands are known to possess an ambidentate nature; in the 3,5-dimethyl-1-(*N*-ethyl)-thiocarbamylpyrazole cobalt(III) complex [31] the ligands bond through the pyrazole ring nitrogen and the thiocarboxamide nitrogen, while in the Ni(II) complex [32] the same ligand coordinates through the pyrazole nitrogen and sulphur from the thiocarboxamide fragment.

The crystallographic asymmetric unit consists of two halves of the [Ni(L-H)$_2$] molecule; there are two centrosymmetric, crystallographically independent half-molecules in the structure, centred at (0, 0, 0) and (1/2, 1/2, 1/2). Two views of the unit cell are shown in Fig. 3.

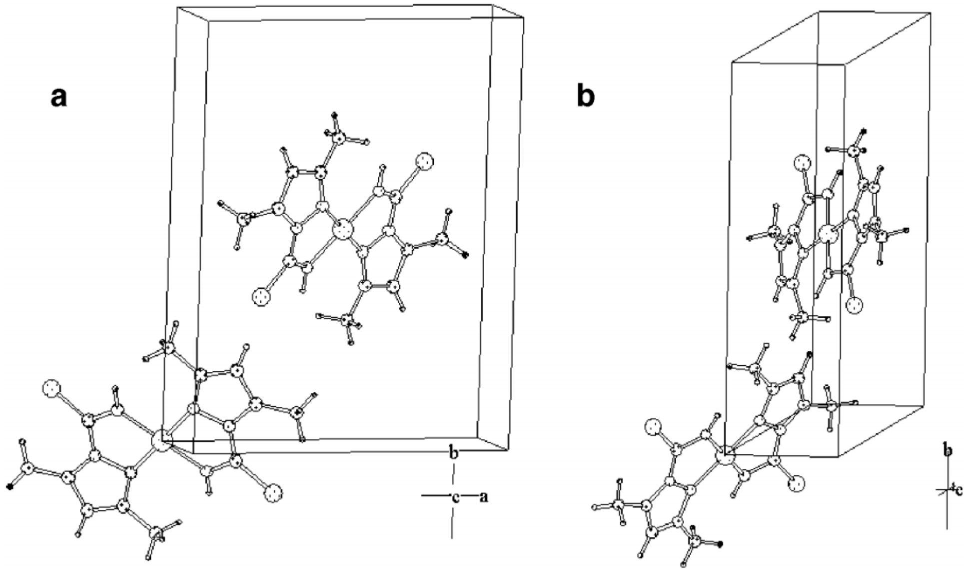

FIGURE 3 Two views of the unit cell for Ni(L-H)$_2$.

TABLE III Selected bond lengths for the complex (Å)

Molecule 1		*Molecule 2*	
Ni(1)–N(2)	1.902(1)	Ni(38)–N(39)	1.9021(8)
Ni(1)–N(3)	1.902(1)	Ni(38)–N(40)	1.9021(8)
N(2)–C(6)	1.35(1)	N(39)–C(43)	1.35(1)
C(6)–N(9)	1.37(1)	C(43)–N(46)	1.37(1)
C(6)–S(14)	1.74(1)	C(43)–S(51)	1.71(1)
N(9)–N(3)	1.40(1)	N(46)–N(40)	1.40(1)
C(17)–N(9)	1.37(1)	C(54)–N(46)	1.39(1)
C(17)–C(16)	1.36(1)	C(54)–C(53)	1.39(1)
C(16)–C(8)	1.35(1)	C(53)–C(45)	1.39(1)
C(8)–C(15)	1.48(1)	C(45)–C(52)	1.50(1)
C(17)–C(26)	1.50(1)	C(54)–C(63)	1.53(1)
C(8)–N(3)	1.36(1)	C(45)–N(40)	1.36(1)

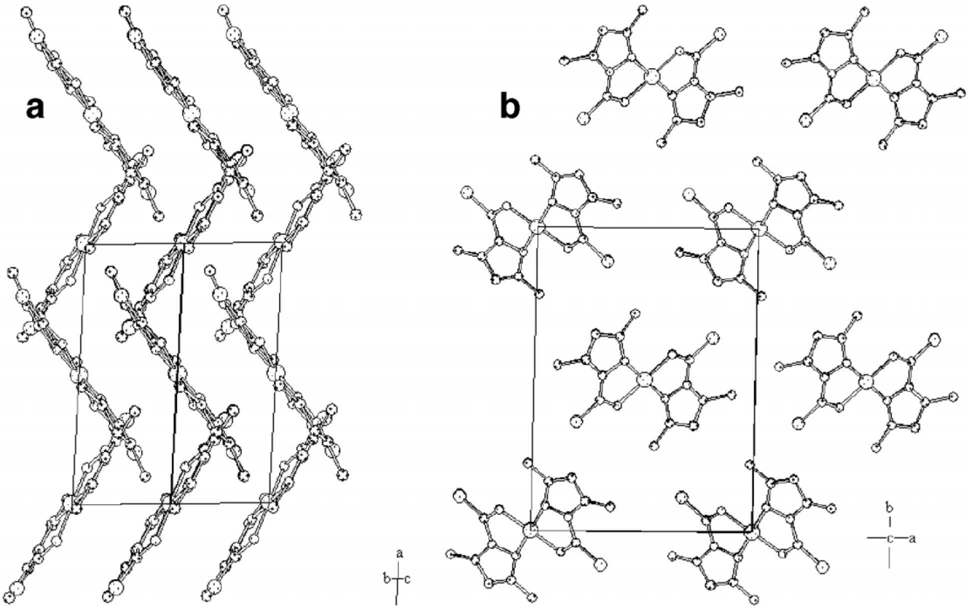

FIGURE 4 Packing diagrams for Ni(L-H)$_2$.

Basic crystallographic data for Ni(L-H)$_2$ are given in Table II and selected bond lengths in Table III. Bond lengths within the two independent molecules are practically identical. Ni–N bond lengths are comparable to those found in the 3,5-dimethyl-1-(*N*-ethyl)thiocarbamylpyrazole Ni(II) complex [32]. Deviations from ideal square-planar geometry can be expressed in terms of the bite angles of the chelate rings. They are 80.8(19) and 99.2(19)° for molecule 1 and 84.0(15) and 96.0(15)° for molecule 2.

Packing diagrams are shown in Fig. 4. While the geometry of the two independent molecules is very similar, they differ in their orientation in the unit cell. The angle between the molecular planes of the two independent complexes is 118°. They form two mutually tilted stacks of parallel molecules arranged in a herring-bone pattern (Fig. 4a). The closest C–H···S contacts between molecules in different columns correspond to H···S distances of 2.66 Å and C–H···S angles of 158°. Within each column, intermolecular distances are determined by the length of the crystallographic *a* axis (4.467 Å). It thus appears that the relative arrangement of the complex molecules in the crystal structure is determined by a combination of weak C–H···S interactions.

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