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Crystal Structure and Spectra of the Ni(II) Complex of Pyridine-2,6-dithio-carbomethylamide

Christoph Kratky[a, *], **Josef Schurz**[a], **Eugen Gagliardi**[b], and **Alois Popitsch**[b]

[a] Institut für physikalische Chemie, Universität Graz, A-8010 Graz, Österreich
[b] Institut für anorganische und analytische Chemie, Universität Graz, A-8010 Graz, Österreich

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The crystal structure of the paramagnetic bis(pyridine-2,6-dithiocarbomethylamide) nickel(II) nitrate (Ni*PDTA*) is described: $C_{18}H_{22}N_6S_4Ni \cdot (NO_3)_2 \cdot (H_2O)_{1.5}$, monoclinic, C2/c, $Z = 4$, $a = 14.705$ (3) Å, $b = 23.254$ (8) Å, $c = 8.383$ (3) Å, $\beta = 98.18$ (2)°, $d_x = 1.55\,\mathrm{gcm}^{-3}$, $d_m = 1.53\,\mathrm{gcm}^{-3}$. The structure was solved with *Patterson* and difference *Fourier* techniques and refined to a residual of $R = 0.053$. The nickel is surrounded by a square bipyramidal coordination of four thioamide sulfur atoms and two pyridine nitrogen atoms. Vibrational and electronic band positions for this compound are discussed.

[Keywords: Crystal structure analysis; Electronic spectra; Infrared spectra; Magnetic susceptibility; Pyridine-2,6-dithiocarbomethylamide nickel(II)]

Kristallstruktur und Spektren des Pyridin-2,6-dithiocarbomethylamid Nickel(II)-Komplexes

Die Kristallstruktur des paramagnetischen bis(Pyridin-2,6-dithiocarbomethylamid) Nickel(II)-nitrats (Ni*PDTA*) wurde bestimmt. $C_{18}H_{22}N_6S_4Ni \cdot (NO_3)_2 \cdot (H_2O)_{1,5}$, monoklin, C2/c, $Z = 4$, $a = 14{,}705$ (3) Å, $b = 23{,}254$ (8) Å, $c = 8{,}383$ (3) Å, $\beta = 98{,}18$ (2)°, $d_x = 1{,}55\,\mathrm{gcm}^{-3}$, $d_m = 1{,}53\,\mathrm{gcm}^{-3}$. Das Phasenproblem wurde mittels *Patterson*- und Differenz-*Fourier*-Synthese bestimmt und die Struktur bis zu einem kristallographischen *R*-Faktor von $R = 0{,}053$ verfeinert. Das Nickel-Atom ist von vier Thioamid-Schwefelatomen und zwei Pyridin-Stickstoffatomen in quadratisch-bipyramidaler Anordnung umgeben. Schwingungsspektren und Anregungsspektren des Komplexes werden diskutiert.

Introduction

IR evidence suggests, that coordination of pyridine-2,6-dithiocarbomethylamide to metal atoms can yield essentially two kinds of complexes[1,2]: the one type has the metal coordinated to the two

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thioamide sulfur atoms and the ring nitrogen atom (SNS), whereas the other type involves the thioamide nitrogen atoms instead of sulfur (NNN). The occurrence of either type depends on the kind of metal atom and on the overall charge of the complex[2]. In the present communication we report the crystal structure analysis of the Nickel-complex (Ni*PDTA*), presumed (from the IR data) to be of SNS type. The structure analysis was carried out to check this assignment and to yield an unambiguous basis for spectroscopically based assignments in other *PDTA* complexes.

Experimental

X-Ray Analysis: Crystals appeared in the form of black prisms. Approximate cell dimensions and the space group were determined from a set of precession photographs. A crystal with approximate dimensions $0.07 \times 0.2 \times 0.2$ mm was used for the subsequent diffractometer measurements, which were carried out on a Nonius Cad-4 diffractometer at the *Eidgenössische Technische Hochschule Zürich*[3]. After least-squares refinement of orientation matrix and cell dimensions with 12 reflections, intensity measurements were made in the ω-scan mode with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å). All reflections within $2\theta < 48°$ ($\sin\theta/\lambda < 0.572$) were recorded, using variable scan speed and a scan width which increased with increasing scattering angle to allow for profile broadening. The 2290 independent reflections were processed to yield 1950 reflections with intensity significantly above background [$|F_0| > 3\sigma(|F_0|)$]. No absorption correction was applied [μ(MoK_α) $= 10.2\,\mathrm{cm}^{-1}$][4].

A sharpened *Patterson* synthesis readily yielded the position of the nickel atom, which, for stoichiometric reasons, had to occupy a position with multiplicity 4. The positions of the remaining non-hydrogen atoms were obtained from a series of difference *Fourier* syntheses. Coordinates and anisotropic temperature factors were refined with full-matrix least-squares techniques for all non-hydrogen atoms except the water molecules (vide infra). In the terminal stages of refinement, hydrogen atoms (at calculated positions) were included in the structure factor calculations, but not refined.

It was apparent from the outset of the structure determination, that the 6 water molecules per unit cell required by the elementary analysis could not be accomodated in an ordered structure in space group $C2/c$. A difference *Fourier* synthesis with a model without water molecules showed 3 peaks per asymetric unit, which were arranged on and near the 2-fold axis. Each of these positions was tentatively occupied with a "half" water molecule with $u = 0.1$ Å^2. In the subsequent refinement, the isotropic temperature factors of these 3 "atoms" were fixed and the population parameters were allowed to refine, together with their coordinates. It turned out that, at the close of the refinement, the sum of the three population parameters did, indeed, add up to approximately 1.5, which is the number of water molecules per asymetric unit predicted by the chemical analysis. The refinement of the above model (180 variables, 1843 contributing reflections, $1/\sigma^2$ weights) converged at a residual of $R = 0.053$. A final difference *Fourier* synthesis showed no peaks higher than $0.5\,e$Å^{-3}.

Spectra and Magnetic Data: Diffuse reflectance spectra at 300 and 80 K were obtained from microcrystalline samples using a Beckmann DK2a spectrometer. Technical details are given elsewhere[5]. Magnetic susceptibility measure-

Table 1A. *Fractional atomic coordinates and vibrational tensor components (× 10^4, U values in Å^2) for the non-hydrogen atoms in the asymetric unit.* The temperature factor is of the form: anisotropic atoms: $T = \exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$ isotropic atoms: $T = \exp[-(8\pi^2U_{iso}\sin^2\theta/\lambda^2)]$. E.s.d.'s (in parentheses) are in units of the last significant figure. Population parameters for H_2O: $*pp = 0.35$; $**pp = 0.29$; $***pp = 0.24$

	x/a	y/b	z/c	U_{11} or U_{iso}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
NI	5000 (0)	1637 (1)	7500 (0)	562 (13)	347 (11)	546 (13)	0 (0)	91 (10)	0 (0)
N1	3834 (8)	2737 (4)	10936 (13)	863 (81)	581 (65)	695 (72)	253 (59)	234 (61	62 (55)
N2	2872 (7)	545 (4)	4884 (12)	654 (69)	578 (62)	596 (64)	7 (53)	—64 (54)	—58 (51)
N3	5000 (0)	2519 (5)	7500 (0)	575 (82)	373 (68)	387 (69)	0 (0)	67 (61)	0 (0)
N4	5000 (0)	758 (5)	7500 (0)	434 (73)	365 (66)	489 (74)	0 (0)	153 (60)	0 (0)
C1	4237 (8)	2453 (5)	9865 (14)	521 (71)	531 (68)	583 (73)	167 (57)	104 (58)	39 (59)
C2	3540 (8)	816 (5)	5786 (13)	452 (64)	532 (66)	475 (65)	17 (54)	57 (53)	—52 (54)
C3	4638 (7)	2816 (5)	8654 (13)	395 (58)	511 (64)	485 (62)	94 (52)	61 (48)	62 (54)
C4	4294 (8)	466 (4)	6670 (14)	500 (64)	415 (58)	513 (64)	14 (53)	136 (52)	—27 (52)
C5	4641 (9)	3405 (5)	8690 (16)	696 (80)	314 (58)	853 (88)	6 (57)	218 (68)	—66 (63)
C6	4272 (9)	—133 (5)	6668 (14)	647 (76)	433 (63)	582 (72)	—2 (59)	100 (58)	—26 (56)
C7	5000 (0)	3700 (7)	7500 (0)	622 (116)	296 (84)	1128 (165)	0 (0)	143 (112)	0 (0)
C8	5000 (0)	—426 (6)	7500 (0)	860 (137)	212 (72)	831 (130)	0 (0)	178 (109)	0 (0)
C9	3395 (11)	2448 (7)	12192 (17)	1103 (122)	841 (101)	681 (91)	222 (91)	472 (87)	108 (79)
C10	2082 (11)	841 (7)	4035 (18)	822 (105)	903 (108)	827 (105)	—12 (87)	—370 (85)	—126 (88)
N (NO_3)	2045 (10)	876 (6)	8860 (19)	1011 (109)	798 (91)	948 (107)	289 (81)	480 (91)	235 (85)
O_1 (NO_3)	1413 (9)	1129 (5)	8043 (15)	1494 (113)	789 (74)	1077 (92)	492 (80)	—5 (82)	—32 (67)
O_2 (NO_3)	2473 (11)	482 (5)	8386 (18)	2308 (166)	864 (83)	1589 (125)	861 (101)	1132 (122)	462 (83)
O_3 (NO_3)	2241 (10)	1019 (8)	10249 (20)	1180 (113)	2359 (191)	1042 (107)	392 (117)	231 (90)	97 (120)
H_2O*	9368 (31)	8 (17)	8747 (40)	1000 (0)					
H_2O**	5000 (0)	5161 (25)	7500 (0)	1000 (0)					
H_2O***	153 (53)	196 (30)	6275 (75)	1000 (0)					

ments were carried out on a SUS 10 instrument (manufactured by A. Paar KG, Graz, Austria), which uses a modified *Faraday* technique[6]. Infrared spectra between 4000 cm^{-1} and 200 cm^{-1} were obtained as nujol mull on a Perkin-Elmer 580B, far infrared spectra were recorded on a Beckmann 725FS instrument.

Table 1B. *Calculated fractional coordinates (× 10^4) for the hydrogen atoms in the asymetric unit*

	x/a	*y/b*	*z/c*
H (N1)	3824	3184	10889
H (N2)	2915	102	4767
H (C5)	4381	3624	9604
H (C6)	3719	−353	6043
H (C7)	5000	4160	7500
H (C8)	5000	−884	7500
H1 (C9)	2871	2166	11554
H2 (C9)	3929	2188	12880
H3 (C9)	3061	2682	13072
H1 (C10)	1765	1066	4957
H2 (C10)	2350	1155	3256
H3 (C10)	1528	617	3286

Results and Discussion

Crystal Structure

Table 1A lists coordinates and vibrational tensor components for all the non-hydrogen atoms in the asymetric unit. Calculated hydrogen positions are listed in Table 1B. Bond lengths and bond angles are given in Fig. 1, and a stereoscopic packing diagram is displayed in Fig. 2.

The structure consists of discrete $Ni(PDTA)_2$ complexes (Fig. 3) arranged on the two-fold axes. Although the crystallographic symmetry around the nickel atoms is therefore only C_2, the $Ni(PDTA)_2$ units show approximate D_{2d} symmetry and the square-bipyramidal coordination of nickel by the 4 thioamide sulfur atoms and the two pyridine nitrogen atoms has approximate D_{4h} symmetry. The packing of the crystal structure appears to be dominated by several hydrogen bonds, which involve the nickel-complex, the nitrate counter ions and the (disordered) water molecules: $H(N2) \ldots O_2(NO_3)_{x,-y,-1/2+z}$: 1,84 Å; $H(N1) \ldots O_1(NO_3)_{1/2-x,1/2-y,2-z}$: 1.89 Å; several contacts of the length expected for a hydrogen bond exist also between the three locations of disordered water molecules and two of the nitrate oxygen atoms (O_1 and O_2).

Bond lengths and angles of the Ni-complex do not show significant deviations from the values observed for the free *PDTA* ligand[7]. This is somewhat surprising, since one might have expected a lengthening of the thioamide C=S bonds as a result of complex formation, which is in fact suggested by the IR-spectroscopic evidence. The main difference between free *PDTA* and its Ni-complex is, of course, the conformation of the thioamide group; while, in the free *PDTA*, the thioamide sulfur atoms are *E* with respect to the pyridine nitrogen, nickel complex formation forces them to be *Z*. However, in both crystal structures, the *PDTA* molecules are nearly planar (Ni-complex: dihedral angles N 3-C 3-C 1 N 1: —176°; N 4-C 4-C 2-N 2: 176°).

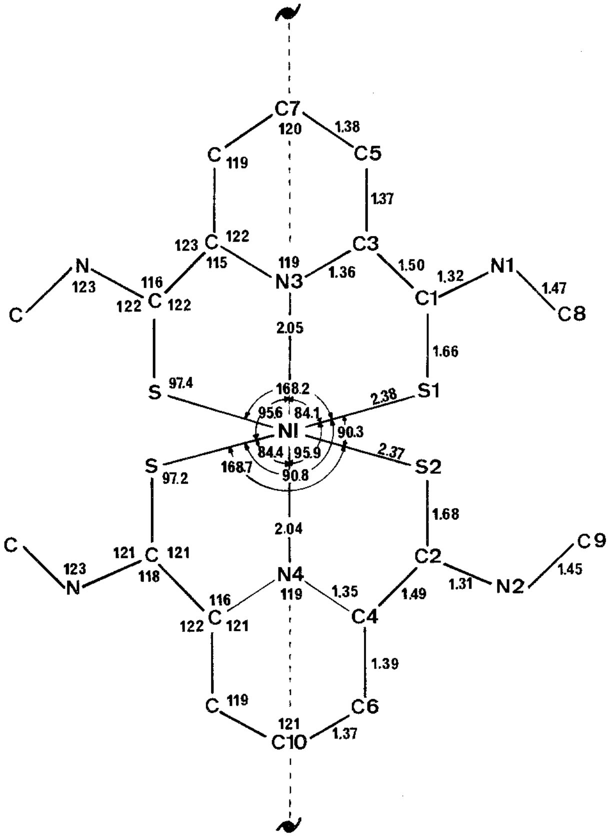

Fig. 1. Bond lengths and bond angles

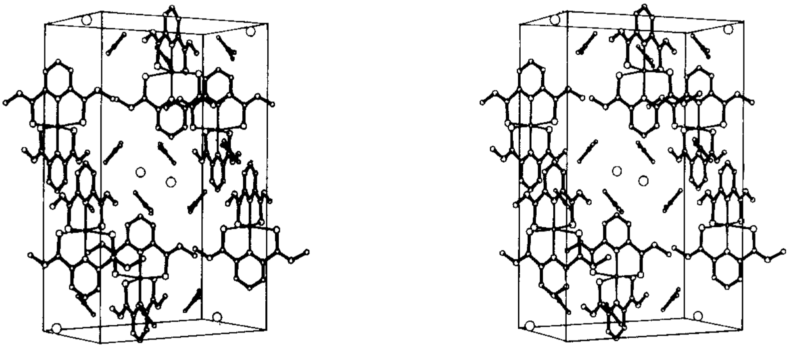

Fig. 2. Stereoscopic packing diagram for the crystal structure of Ni-*PDTA*. Hydrogen atoms are omitted

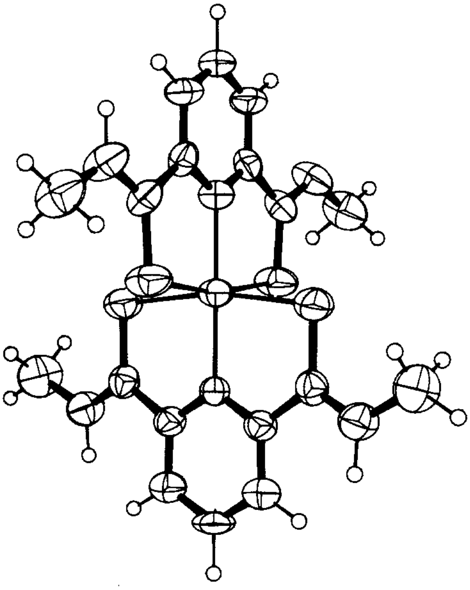

Fig. 3. Ortep-drawing of the Ni($PDTA$)$_2$ unit. Ellipsoids are drawn at the 50% probability level

The overall shape of the Ni($PDTA$)$_2$ complex is quite similar to the corresponding complex of the pyridine-2,6-dicarboxylic acid[8]. Although the coordination around nickel in the present crystal structure is clearly square-bipyramidal, the distribution of bond lenghts between nickel and its coordinating atoms suggests, that a certain amount of distortion towards a square-planar nickel coordination exists: values between 2.16 and 2.25 Å are observed for the Ni—S distance in square-planar NiS_4 systems[9], while the Ni—S distances in the crystal structure of bisthioureanickel(II) thiocyanate[10] [square-bipyramidal coordination around Ni(II)] are between 2.53 and 2.56 Å. Likewise, the distances from nickel to the pyridine nitrogen atoms are longer than in related structures [1.95—1.98 Å in Ni(II)-pyridine-2,6-dicarboxylic acid[8] and 1.99 Å in bisthioureanickel(II) thiocyanate[10]].

Table 2. *Observed band positions, assignments (based on assumed* D_{4h} *symmetry), and calculated transition energies for the electronic spectra of PDTA and* Ni-*PDTA*. All values are given in kK. Numbers in parentheses indicate log ε ($mol^{-1}\,cm^{-1}\,l$).

Transition Energies					Assignment
A	B	C	D	E	
		9.6	9.8	9.8	$^3B_{1g} \rightarrow {}^3B_{2g}\,(^3T_{2g})$
	11.9 (1.96)	12.3	12.4	12.4	$^3E_g\,(^3T_{2g})$
			15.4		$^1B_{1g}\,(^1E_g)$
			16.1	16.2	$^3A_{2g}\,(^3T_{1g}, F)$
	18.1 (2.43)	18.5	18.5	18.9	$^3E_g\,(^3T_{1g}, F)$
	21.3 (2.65)	23.3	23.8		$^1B_{2g}\,(^1T_{2g})$
24.9 (2.6)		25.3			$^1A_{1g}\,(^1A_{2g})$
		27.0			$^1A_{2g}\,(^1T_{1g}), {}^1E_g\,(^1T_{2g})$
			29.2	29.4	$^3E_g\,(^3T_{1g}, P)$
	30.3 (4.25)	30.6	30.9	30.7	$^3A_{2g}\,(^3T_{1g}, P)$
31.0 (4.4)	34.7 (4.34)		33.9		
	40.7 (4.39)		35.8		
41.2 (4.4)			40.5		

A, B: Electronic absorption (in ethanol) of the free *PDTA* ligand (A) and its nickel complex (B).

C, D: Diffuse reflectance spectra at 300 K (C) and at 80 K (D).

E: Calculated transition energies, using the parameter values $B = 875\ cm^{-1}$; $D_q = 975\ cm^{-1}$; $Dt = -306\ cm^{-1}$; $Ds = 830\ cm^{-1}$[12].

Electronic Spectra and Magnetic Measurements

The diffuse reflectance spectra (80 K) can be satisfactory interpreted in terms of a D_{4h} microsymmetry around Ni(II). The assignment (Table 2) was derived from a comparison with the relevant *König-Kremer*[11] energy level diagram. Crystal field parameters in the zero spin-orbit interaction approximation were calculated for the 6 spin-allowed transitions[12]. "Best" values for B, D_q, Dt and Ds were obtained by a weighted least-squares fit of calculated to observed (80 K) band positions; they reproduce the observed positions within experimental error (Table 2). Spin-forbidden transitions were not used in this calculation; their assignment in Table 2 is based only on the *König-Kremer* table.

Table 3. *Magnetic susceptibility of* Ni-*PDTA*

Temperature K	Magnetic Susceptibility[a] × 10^{-3} emu/mol	Magnetic Moment[b] B.M.
299.4	3.83	2.98
278.7	4.11	2.97
248.4	4.60	2.96
220.0	5.15	2.94
181.8	6.20	2.90
169.1	6.64	2.90
144.3	7.70	2.88
118.8	9.18	2.83
92.2	11.56	2.76
79.3	13.24	2.71

[a] Obtained at 4 different field strengths: 1.21, 0.91, 0.71 and 0.41 Tesla. All values are corrected[13] to correspond to the magnetic susceptibility of Ni(II), using the following dimagnetic correction susceptibilities (in 10^{-6} emu/mol): Ni^{2+}: —11.0; NO_3^-: —20.0; H_2O: —14.0; field dependent diamagnetic corrections had to be used for the ligand: the corrections (for the above strengths) are —92.0, —85.2, —68.8 and —29.8, respectively. The corrected paramagnetic susceptibilities showed no dependence on field strength.

[b] Calculated as $2.83\sqrt{\chi(T-\theta)}$. ($\chi$: corrected magnetic susceptibility, θ: *Curie-Weis* temperature, $\theta = -10$ K).

In solution at room temperature, only 3 broad bands are observed at somewhat lower energies than in the crystal. It is therefore not possible to derive the D_{4h} crystal field parameters for the Ni(*PDTA*)$_2$ complex in solution; however, the occurrence of 3 bands excludes the existence of square-planar nickel. This is in agreement with the magnetic measurements (Table 3), which indicate a high-spin configuration. The observed magnetic susceptibility decreases slightly with decreasing temperature, and the magnetic moment is at the lower end of the range expected for 6-coordinated nickel(II)[13].

Infrared Spectra

The correspondence of observed band positions in the thioamide IR frequencies of Ni *PDTA* (Table 4) and the free ligand is quite consistent with their crystal structures. Thus, the hypsochromic shift of νCN is explainable by an increase in C = N double bond character as a result of the formation of Ni—S bonds. Bands with NH contribution suffer a bathochromic shift, partly for the above reason, partly as a result of the formation of hydrogen bonds. Bands with considerable CS contribution should also be expected to show a bathochromic shift; however, the coupling with the (hypsochromically shifted) CN and CS band appears to outbalance this effect and only minor shifts are observed. The assignment given for the far IR region to νNiN and νNiS (Table 4) is based on a comparison with the relevant literature[14].

Table 4. *Observed IR frequencies for* Ni-*PDTA*. Observed as nujol mulls, with the exception of frequencies marked with a cross (+), which were observed from a KBr disc

3180 s (νNH), 3070 s (νNH), 2965^+ s, 2930 s, 1595 m, 1562 s (νCN + δNH), 1480^+ m, 1438^+ m, 1420 m, 1365^+ vs ($\nu_{as}NO_3$), 1322 vs, 1291 s (δNH + νCN), 1252 m, 1192 w, 1154 w, 1058 s, 1045 sh, 1030 w, 1012 s, 945 s (νCS + νCC), 928 w, 831 sh (δNO_3), 824 s (νCS?), 768 m, 755 m, 673 s (δNCS), 630 m (o.o.p.NH), 617 m, 550 s, 390 m, 370 m, 312 s (νNiN), 280 m (νNiS), 258 w, 234 w, 205 s, 162 m, 143 m.

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