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Synthesis and Molecular Structure of a Pentacoordinated Nickel(II) Complex with a Mixed S_2N_3 Coordination Sphere

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Introduction

Nickel is known to be an essential trace element for bacteria, plants, and animals. Four different types of enzymes incorporate this transition metal in their active center. Recently, more definitive information is available on the precise coordination geometry of the metal center in these enzymes.[1,2] Several donor atom sets (e.g. S_4, N_4) and geometries (e.g. tetragonal planar, tetrahedral, trigonal bipyramidal) are known to occur in natural Ni-containing systems. In addition to coordination spheres consisting mainly of nitrogen donor atoms, sulfur ligands play an important role in the bioinorganic chemistry of this element. Therefore, the synthesis of new Ni(II) complexes with a sulfur-containing donor atom set represents a field of continuing interest. Other than the composition of the coordination sphere, the geometrical constraints of the polypeptide backbone on the metal center are of considerable importance for the properties of a metal-centered system.

With this background we were encouraged to develop a ligand system inducing high constraints on a Ni(II) center, which additionally leaves free coordination sites for ligand exchange reactions. The amine nitrogen of the tridentate dibasic S_2N ligand shown in Figure 1 potentially favors a facial over a meridional coordination type on metal complexes. The synthesis and chelating effect of the novel tridentate ligand $(HSC_6H_4)_2NCH_3$, **4**, on a Ni(II) center is discussed in detail in this paper.

Experimental Section

Materials and Spectroscopy. All manipulations were performed under argon using standard Schlenk techniques. Solvents, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), and *N*-methyldiphenylamine were deaerated, dried, and distilled before use. Reagents were AR grade or above and were purchased from Nacalai Tesque Inc. and Wako Chemicals. IR spectra were obtained on a Shimadzu FTIR-8200D; UV/vis spectra, on a JASCO Model V-570 UV/VIS/NIR; and NMR spectra, on a JEOL JNM-EX270.

$(HSC_6H_4)_2$-N-CH_3, (4, LH_2). To a stirred solution of 69.3 mmol *n*-butyllithium (43.3 mL of 1.6 M in hexane) in 100 mL of cyclohexane and 6.5 g (55.9 mmol) of TMEDA was added slowly 5.08 g (27.72 mmol) of diphenylmethylamine at 0 °C. The clear yellow solution was stirred for 8 days at room temperature. To the cooled (−20 °C) yellow orange solution was added 2.1 g of elementary sulfur. After 24 h of stirring at room temperature the white precipitate, **3**, was filtered and washed twice with 50 mL pentane. ^{1}H-NMR **3** (DMSO-d_6): 7.13 (d, 2H), 6.59 (d, 2H), 6.53 (t, 2H), 6.47 (t, 2H), 2.96 (s, 3H, NC*H*$_3$), 2.27(4H, C*H*$_2$-TMEDA), 2.10 (12H, C*H*$_3$-TMEDA). ^{13}C-NMR **3** (DMSO-d_6): 151.62 (s), 134.92 (d), 129.49 (s), 122.48 (d), 120.76 (d), 117.83 (d), 57.16 (t, *C*H$_2$-TMEDA), 45.52 (q, *C*H$_3$-TMEDA), 39.97 (q, N*C*H$_3$). Water (100 mL) was added to **3**, and the white suspension was extracted twice with 50 mL of diethyl ether. The aqueous phase was brought to pH 5 by adding slowly 0.1 M HCl. The clear yellow solution was extracted twice with 50 mL of diethyl ether. This organic fraction was dried over $MgSO_4$, and the solvent, evaporated. The yellow-white oily residue was crystallized from diethyl ether at −20 °C, forming white crystals of **4** in 65% yield. ^{1}H-NMR (ppm, $CDCl_3$): 7.29 (d, 2H), 7.11 (t, 2H), 6.99 (t, 2H), 6.97 (d, 2H), 3.80 (s, 2H, S*H*), 3.13 (s, 3H, NC*H*$_3$). ^{13}C-NMR (ppm, $CDCl_3$): 147.04 (s), 130.49 (d), 128.81 (s), 126.29 (d), 124.49 (d), 122.84 (d), 40.20 (q, N*C*H$_3$). IR (cm^{-1} in KBr): 3055.0 (w), 2962.5 (w), 2526.6 (w), 1577.7 (m), 1471.6 (vs), 1261.4 (s), 1083.9 (s), 804.3 (m), 750.3 (s).

$[Ni^{II}L]_n$, (5). The free ligand **4** (0.31 g; 1.25 mmol) dissolved in 10 mL of diethyl ether was added to $Ni(acac)_2$ (0.32 g). After stirring the suspension for 6 h at 23 °C the resulting fine black precipitate was collected by filtration and washed three times with 5 mL of cold (0 °C) diethyl ether. The product was dried under high vacuum for 2 h, yielding 0.34 g of **5**. IR (cm^{-1} in KBr): 3051.2 (w), 1575.7 (m), 1458.1 (vs), 1114.8 (m), 754.1 (vs).

$Ni^{II}[((CH_3)_3CC_5H_4N)_2((SC_6H_4)_2NCH_3)]$ (6). To a suspension of **5** (0.16 g, 0.53 mmol) in diethyl ether (10 mL) was added 0.20 g of 4-*tert*-butylpyridine. The dark brown color of the suspension changed to light greenish brown. The reaction mixture was allowed to stir for 4 h. After evaporation of half of the solvent, the solid was collected by filtration, washed with 10 mL of pentane, and dried under high vacuum. Yield: 2.87 g, 0.50 mmol, 94% (*M* = 574.49 g/mol). Anal. Calcd for $C_{31}H_{37}N_3S_2Ni$: C, 64.81; H, 6.49; N, 7.31. Found: C, 65.38; H, 6.51; N, 6.94. UV/vis (nm (M^{-1} cm^{-1}), in CH_2Cl_2): 229 (11000), 290 (7800), 450 (800), 530 (410). IR (cm^{-1} in KBr): 3049.2 (w), 2968.2 (s), 2869.9 (w), 1701.1 (vs), 1458.1 (vs), 1419.5 (s), 1224.7 (m), 1068.5 (s), 839.0 (m), 831.3 (m), 769.9 (m), 754.1 (m). Crystallization was successful by slow evaporation of the toluene solution at 8 °C in air or by slow cooling of a concentrated toluene−pentane solution (10:1) to −25 °C.

Crystallography. All measurements of **6** were made on a Rigaku AFC5R diffractometer with graphite monochromatic Mo Kα radiation and a 12 kW rotating anode generator. Calculations were done using the TEXSAN program package. The structure was solved by direct methods[3] and expanded using Fourier techniques.[4] The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically; the rest were included at fixed positions. The final cycle of full-matrix least-squares refinement was based on 2249 observed reflections and 346 variable parameters. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.35 and −0.26 e/Å^3, respectively. Machine parameters, crystal data, and data collection parameters are listed in Table 1. Positional parameters of non-hydrogen atoms are listed in Table 2, and selected distances and angles in Table 3.

Results and Discussion

The newly developed ligand **4** is synthesized via double *ortho*-lithiation. The lithiation of monoarylamines and phosphines has been reported.[5] No detailed report on di- or triaryl

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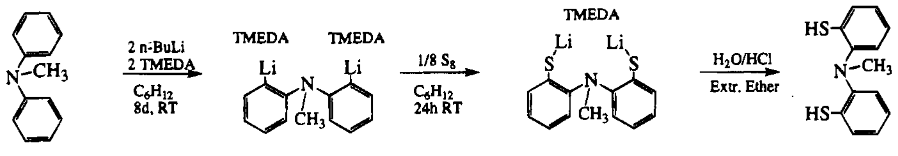

1 2 3 4

Figure 1. Synthesis of bis(2-mercaptophenyl)-*N*-methylamine, **4**.

Table 1. Crystal Data, Experimental Details, and Refinement Parameters for $Ni^{II}L$(4-*tert*-butylpyridine)$_2$ (**6**)

empirical formula	$C_{31}H_{37}N_3S_2Ni$
fw	574.47 g/mol
crystal system	triclinic
a	11.750(4) Å
b	12.951(6) Å
c	10.713(8) Å
α	110.64(4)°
β	94.90(5)°
γ	99.07(4)°
V	1488(1) $Å^3$
space group	$P\bar{1}$ (No. 2)
Z	2
D_{calc}	1.281 g/cm^3
radiation	Mo Kα (λ = 0.71069 Å) graphite monochromator
μ(Mo Kα)	8.16 cm^{-1}
temp	23.0 ± 1°C
R^a	0.044
$R_w{}^a$	0.047

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2]^{1/2}$.

Table 2. Positions and Thermal Parameters of Atoms for **6**

atom	*x*	*y*	*z*	*B*(eq)[a] ($Å^2$)
Ni(1)	0.33944(8)	0.22624(7)	0.29847(9)	3.64(2)
S(1)	0.2690(2)	0.0752(2)	0.0968(2)	4.74(5)
S(2)	0.2829(2)	0.3374(2)	0.4895(2)	4.93(5)
N(1)	0.3129(4)	0.0946(4)	0.3871(5)	3.3(1)
N(2)	0.5145(4)	0.2447(4)	0.3150(5)	3.6(1)
N(3)	0.3299(5)	0.3510(4)	0.2167(5)	3.7(1)
C(1)	0.1752(5)	0.0063(5)	0.1751(6)	3.5(2)
C(2)	0.2007(5)	0.0233(5)	0.3123(6)	3.1(2)
C(3)	0.1214(6)	−0.0259(6)	0.3733(6)	3.9(2)
C(4)	0.0184(6)	−0.0959(6)	0.2989(8)	4.9(2)
C(5)	−0.0060(6)	−0.1162(6)	0.1633(8)	5.1(2)
C(6)	0.0719(7)	−0.0660(6)	0.1034(6)	4.4(2)
C(7)	0.2958(5)	0.2554(6)	0.5870(7)	4.1(2)
C(8)	0.3142(5)	0.1457(6)	0.5336(7)	3.8(2)
C(9)	0.3312(6)	0.0864(6)	0.6165(7)	5.2(2)
C(10)	0.3302(7)	0.135(1)	0.7539(9)	6.6(3)
C(11)	0.3105(8)	0.240(1)	0.8067(9)	7.3(3)
C(12)	0.2941(7)	0.3006(7)	0.7270(8)	6.0(2)
C(13)	0.4051(7)	0.0261(7)	0.3554(9)	4.4(2)
C(14)	0.2263(6)	0.3525(5)	0.1584(7)	4.2(2)
C(15)	0.2035(6)	0.4376(6)	0.1174(7)	4.5(2)
C(16)	0.2898(6)	0.5276(5)	0.1309(6)	3.8(2)
C(17)	0.3989(6)	0.5246(6)	0.1897(7)	4.5(2)
C(18)	0.4141(6)	0.4375(6)	0.2304(7)	4.8(2)
C(19)	0.2718(7)	0.6241(6)	0.0859(8)	5.2(2)
C(20)	0.297(1)	0.7324(8)	0.207(1)	13.7(5)
C(21)	0.148(1)	0.612(1)	0.029(2)	15.8(6)
C(22)	0.349(1)	0.633(1)	−0.012(1)	15.3(6)
C(23)	0.5707(6)	0.1827(6)	0.2212(7)	4.4(2)
C(24)	0.6893(6)	0.1887(6)	0.2385(7)	4.2(2)
C(25)	0.7590(6)	0.2609(6)	0.3567(7)	3.9(2)
C(26)	0.7002(6)	0.3263(6)	0.4516(7)	5.1(2)
C(27)	0.5824(6)	0.3165(6)	0.4282(7)	4.8(2)
C(28)	0.8907(6)	0.2720(6)	0.3797(8)	4.7(2)
C(29)	0.9231(8)	0.1579(9)	0.318(1)	10.5(3)
C(30)	0.9453(8)	0.350(1)	0.318(1)	10.9(4)
C(31)	0.9409(7)	0.316(1)	0.528(1)	9.0(3)

[a] $B(eq) = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + U_{12}(aa^*bb^*)\cos\gamma + U_{13}(aa^*cc^*)\cos\beta + U_{23}(bb^*cc^*)\cos\alpha)$.

Table 3. Selected Distances and Angles for **6**

atoms	angle (deg)	atom	distance (Å)
S(1)Ni(1)S(2)	142.4(1)	Ni−S(1)	2.320(3)
S(2)Ni(1)N(2)	111.9(2)	Ni−S(2)	2.272(2)
S(1)Ni(1)N(2)	104.8(2)	Ni−N(1)	2.221(5)
N(1)Ni(1)N(3)	168.8(2)	Ni−N(2)	2.018(5)
N(2)Ni(1)N(3)	95.3(2)	Ni−N(3)	2.104(5)
S(1)Ni(1)N(3)	95.4(2)		
S(2)Ni(1)N(3)	89.4(2)		
N(2)Ni(1)N(1)	95.8(2)		
S(1)Ni(1)N(1)	83.4(1)		
S(2)Ni(1)N(1)	85.0(1)		

phosphines, amines, or thioethers is known. Dilithiation of *N*-methyldiphenylamine yielded the bis-*ortho*-lithiated product **2**. The triple lithiation of triphenylamine by the same method failed and resulted in a mixture of mainly *meta*-substituted compounds. The high yield (95%, determined by quenching of the reaction mixture with D_2O) *vs* the amine makes **2** a versatile reagent for consequent electrophilic attack. Addition of elementary sulfur produces the dilithium dithiolate, **3**, which precipitates as a white powder from cyclohexane. ^1H-NMR data indicate the presence of only 1 equiv TMEDA per dithiolate. Thus, the presence of only 2.5 donor atoms per lithium cation indicates an oligomeric structure of the dilithium salt. Protonation of **3** results in the formation of the desired thiolate ligand, **4**. The second step in this synthesis reduces the overall yield of **4** to 60%. Probably the excess of butyllithium in the reaction mixture results in formation of other lithiated products after addition of the electrophile. Separation from bad smelling side products can be accomplished by successive extraction methods, chromatography, and crystallization.

Reaction of **4**, LH_2, with $Ni(acac)_2$ in ethanol yields almost quantitatively a dark brown, almost black, material with the composition $(NiL)_n$ (**5**). From mass spectroscopic methods no information about the molecular mass of the compound could be obtained. We believe that this compound exhibits a polymeric structure, which is confirmed by broad signals in the IR spectrum (KBr pellet). Only polar or coordinating solvents are able to solubilize the compound easily, another indication for higher nuclearity of **5**. Addition of 4-*tert*-butylpyridine (*t*-bupy) to a suspension of **5** in diethyl ether affords a greenish-brown solid, characterized as Ni(L)(*t*-bupy)$_2$, **6**. Satisfactory elementary analysis was obtained. This compound is soluble in a wide range of solvents, from cyclohexane to dimethylformamide, and can be recovered undecomposed by precipitation from the solution by adding water or pentane depending on the solvent.

X-ray diffraction analysis of a crystal of **6** shows that the nickel center is coordinated in a trigonal bipyramidal (tbp) arrangement. Both ligand sulfur atoms and the N atom of one *tert*-butylpyridine unit occupy the equatorial positions, whereas the ligand nitrogen atom and the other pyridine ligand are found in the apical coordination sites. A PLATON plot of the molecule is shown in Figure 2. The nickel lies exactly in the equatorial plane S(1)−S(2)−N(2) (the sum of angles is 359.1°). However, the S−Ni−S angle of 142.4(1)° deviates considerably from the ideal 120°. The two apical positions are bent both *ca.* 5.5° toward the two sulfur atoms in the equatorial plane.

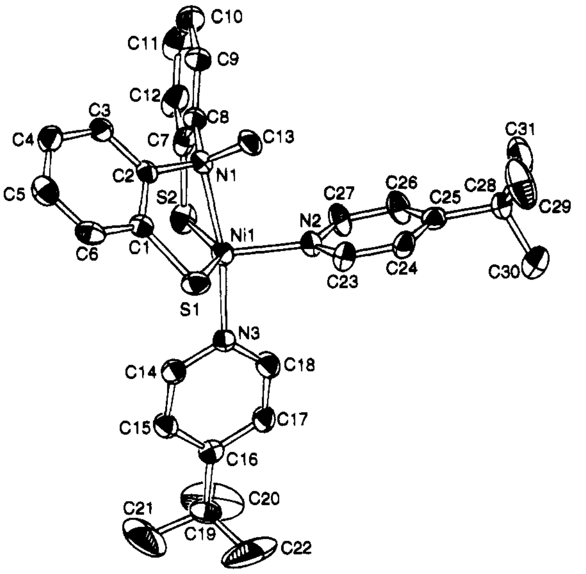

Figure 2. PLATON plot of **6** with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

The bond angle N(1)−Ni−N(3)-axis is 168.8(2)°. The ligand itself exhibits a slight unsymmetrical geometry with respect to the sulfur atoms. Their difference in bond length to the nickel center is 5 pm, and the angles S(1,2)−Ni−N(1) differ by 1.6°. This may be an indication for a fluctional coordination behavior of the coordinated ligand in solution. Additionally, the bond length (in Å) of the nitrogen N(1) to the metal center is one of the longest observed so far on Ni(II) complexes, which is a result of the weak basicity of the amines and the constraints by the ligand geometry.

A similar coordination type for Ni(II) was observed in the air sensitive complexes with monodentate thiophenolates, Ni(terpyridine)(SAr)$_2$ (SAr = $SC_6H_2Pr^i{}_3$-2,4,6, $SC_6H_3Me_2$-2,6),[6] [Ni(DAPA)(SPh)$_2$]CH_3CN,[7] and an alkanethiolate complex, Ni[{$SCH_2C(Me){=}N(CH_2)_3$}$_2$NH].[8] Normally, five-coordinate Ni(II) complexes are expected in the square pyramidal(sp) geometry.[9−12]The tbp coordination observed in the terpyridine[6] complexes was said to derive from steric hindrance at the thiolate ligands. By contrast, we believe the tbp geometry observed in complex **6** results from coordination constraints imposed by the ligand.

Thiolate atoms are always found in the equatorial plane of the tbp with Ni−S distances around 2.3 Å. The large S−Ni−S angle of 142.4° is the dominating feature in complex **6** which presumably prevents the Ni(II) center from distorted octahedral coordination. The steric hindrance, responsible for the tbp coordination geometry in the complexes described in refs 6−8, is not required.

These structural features should be an indication for a highly reactive and air sensitive compound. Surprisingly, suitable crystals for X-ray analysis were obtained by evaporation from the toluene solution over several days in air. Decomposition reactions take place slowly only after several days, in solution in air, and at room temperature.

Compound **6** exhibits, similar to comparable thiolate ligated tbp-Ni(II) complexes, a high-spin electronic configuration. This paramagnetism is reflected by broad signals in the ^{1}H-NMR spectrum. However, no important shifts to low-field frequencies are observed. One broad signal in the domain from 8.5 to 6 ppm overlaid by some sharper signals can be assigned to aromatic proton resonances. At 3.6 ppm one sharp signal is observed, corresponding to the chemical shift of the methyl group on the amine nitrogen. Furthermore, one very intense broad signal at 1.6 ppm can be assigned to the 18 protons of the two pyridine units.

Mass spectrometric analysis (FAB$^+$ mode) of **6** shows a pyridine-free binuclear derivative with the composition [Ni(L)]$_2$ at *m/z* 608 with the correct isotopic pattern. Additional peaks assigned to the successive fragmentation of the dimer are observed at *m/z* 591, 578, 361, and 213. Even by different mass spectrometric methods (EI, CI), no Ni-containing species were detected.

Our synthetic efforts and structural results show clearly the chelating effect of the ligand **4** on the Ni(II) center. Studies testing reactivity and catalytic activity of **6** and derivatives are on the way as well as the characterization of similar compounds containing different metal centers.

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Supporting Information Available: Tables of complete crystal data, hydrogen atom coordinates and isotropic thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and bond distances and angles (18 pages). Ordering information is given on any current masthead page.

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