Bis(3,5-dimethylpyrazole-1-carbodithioato) Nickel(II) and Its Transformation to a Dinuclear Complex: Crystal Structure of $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$ (L^1 = 3,5-dimethylpyrazole-1-carbodithioate)[†]

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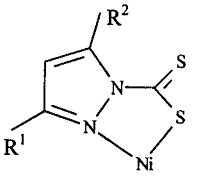
Introduction

Nickel(II) complexes in N_2S_2 environments with open sites are useful in establishing the ligand and coordination environment about the nickel center in the α-metallosubunit of carbon monoxide dehydrogenase (CODH) as examined by XAS.[1] The redox and magnetic properties of the nickel center is very much dependent on the nature of the ligands and the coordination environment. In a square planar ↔ tetrahedral equilibrium situation both the steric crowding and electronic effects are important in generating a particular geometry. The mononuclear NiN_2S_2 complexes of bidentate N,S donor ligands show interesting structural, magnetic, and electrochemical properties and are relevant to the active site geometries of CODH.[2] The coordination properties of the ambidentate pyrazoledithiocarboate ligands and a preferential five-membered N,S chelate ring (I) formation compared to a four-membered S,S ring (II) has been known for some years.[3] The chemistry of sulfur-ligated nickel oxidation states has attracted a great deal of attention in recent years.[4] The complexation behavior of nickel by the simple dithiocarbamate ligands of secondary amines give the diamagnetic bis(dithiocarbamate) chelate $Ni^{II}(dtc)_2$.[5] In solution bis(3,5-dimethylpyrazole-1-carbodithioato)nickel(II), $Ni(L^1)_2$ undergoes a facile spontaneous decomposition affording a saddle-shaped dimeric complex $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$ following irreversible CS_2 loss from the 3,5-dimethylpyrazole-1-carbodithioate ligand. The X-ray structure of the neutral dimer is reported and its probable mode of formation suggested.



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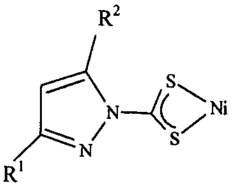

II

Experimental Section

Materials. The chemicals used were obtained from commercial sources. The solvents and reagents used were of reagent grade and used as received without further purification.

3,5-Dimethylpyrazole, 3-phenylpyrazole, and 3-phenyl-5-methylpyrazole were synthesized according to reported procedures.[6−9] Four pyrazole dithiocarboate ligands (KL^1−KL^4; R^1, R^2 = Me, Me; Ph, Me; Ph, H; H, H) were synthesized as their potassium salts following a modified Trofimenko[2a] route from corresponding pyrazoles, KOH and CS_2 in tetrahydrofuran. One representative case is described below. Purification of dichloromethane and dimethylformamide and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.[10]

Preparation of Potassium 3,5-Dimethylpyrazole-1-carbodithioate, KL^1. To a mixture of 3,5-dimethylpyrazole (970 mg, 10.0 mmol) in tetrahydrofuran (15 mL) and finely powdered KOH (580 mg, 10.3 mmol) taken in a mortar was added CS_2 (990 mg, 13.0 mmol) dropwise while stirring and agitating the solution. The solution turned yellow to orange and a heavy mass separated which was immediately filtered off in a G3 frit and thoroughly washed with diethyl ether and dried in vacuo over P_4O_{10}. Yield: 87%. Anal. Calcd for $C_6H_7N_2S_2K$: C, 34.26; H, 3.35; N, 13.32. Found: C, 34.41; H, 3.39; N, 13.42%.

The complexes $[Ni(L^n)_2]$, $n = 1-4$ have all been synthesized in good yields from direct stoichiometric reactions between the ligands and $NiCl_2{\cdot}6H_2O$ in aqueous media.

Preparation of Bis(3,5-dimethylpyrazole-1-carbodithioato)nickel(II), NiL^1_2. An aqueous solution (15 mL) of $NiCl_2{\cdot}6H_2O$ (480 mg, 2.0 mmol) was added dropwise to a magnetically stirred aqueous (20 mL) solution of KL^1 (850 mg, 4.0 mmol). The orange solution immediately turned red, and a dark red compound gradually separated. Stirring was continued for 1 h, and the compound was filtered off, washed with cold water and hexane, and dried in vacuo over P_4O_{10}. Yield: 78%. Anal. Calcd for $C_{12}H_{14}N_4S_4Ni$: C, 35.94; H, 3.49; N, 13.98. Found: C, 35.85; H, 3.45; N, 12.00%. NiL^2_2: Anal. Calcd for $C_{22}H_{18}N_4S_4Ni$: C, 50.30; H, 3.43; N, 10.67. Found: C, 50.10; H, 3.38; N, 10.75%. NiL^3_2: Anal. Calcd for $C_{20}H_{14}N_4S_4Ni$: C, 48.32; H, 2.82; N, 11.27. Found: C, 48.45; H, 2.70; N, 11.45%. NiL^4_2: Anal. Calcd for $C_8H_6N_4S_4Ni$: C, 27.85; H, 1.74; N, 16.25. Found: C, 27.70; H, 1.82; N, 16.07%.

Physical Measurements. Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Indian Association for the Cultivation of Science, Calcutta with a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 883 spectrometer with samples prepared as KBr pellets. Electronic spectra were recorded on a Shimadzu UV 3100 spectrophotometer. Solution electrical conductivity was measured using a Unitech UI 31C digital conductivity meter with a solute concentration of about 10^{-3} M. Magnetic susceptibilities in the solid state were measured with a Gouy balance

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[†] Dedicated to Prof. A. Chakravorty on the occasion of his 65th birthday.

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Table 1. Crystallographic Data for [$Ni_2(\mu$-3,5-$Me_2Pz)_2(L^1)_2$]

empirical formula	$C_{22}H_{28}Ni_2N_8S_4$
fw	650.18
space group	monoclinic *P*21/*n*
a, Å	8.748(2)
b, Å	13.575(3)
c, Å	23.378(5)
β, deg	94.81(3)
V, $Å^3$	2766.5(11)
Z	4
ρ_{calcd}, g cm^{-3}	1.561
F(000)	1344
λ, Å	0.71073
crystal size, mm	0.22 × 0.14 × 0.12
T, °C	17
μ, mm^{-1}	1.691
R^a	0.084
$R_w{}^b$	0.090
GOF	1.45

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

fitted with a polytronic d.c. power supply and a PAR 155 vibrating sample magnetometer. All magnetic moments are corrected for diamagnetism using Pascal's constants.[11] Electrochemical measurements were made using the PAR model 173 potentiostat, 175 universal programmer, 178 electrometer, and 377 cell system. A Digital Electronics series 2000 omnigraphic recorder was used to trace the voltammograms. All electrochemical experiments were performed under a pure dry nitrogen atmosphere. A planar Beckman 39273 platinum-inlay-working electrode, a platinum-wire auxiliary electrode, and an aqueous calomel electrode (SCE) were used in a three-electrode configuration. All electrochemical data were collected at 298 K and are uncorrected for the junction contributions.

Crystallography of Bis(3,5-dimethylpyrazole-1-carbodithioato)-bis(*μ*-3,5-dimethylpyrazolato)dinickel(II), [$Ni_2(\mu$-3,5-$Me_2Pz)_2(L^1)_2$]. Red-brown single crystals were grown by slow diffusion of *n*-hexane into a dichloromethane solution of $NiL^1{}_2$ during 15 d. These crystals were then analyzed. IR (KBr disk): ν_{pz}(ring) 1583, $\nu_{C=S}$ 1342, 886 cm^{-1}. Anal. Calcd for $C_{22}H_{28}N_8S_4Ni_2$: C, 40.64; H, 4.34; N, 17.23. Found: C, 40.55; H, 4.31; N, 17.30%. Selected crystal data and data collection parameters are given in Table 1. The intensity data of the complex were collected on a Rigaku RAXIS IIC imaging-plate diffractometer using a red-brown crystal mounted on a quartz fiber. Unit-cell parameters were calculated from least-squares fitting of the 2*θ* angles for 25 selected strong reflections. The structure was solved by the direct method. Total number of reflections collected is 5064, and the number of independent reflections is 5064. After refinement with isotropic thermal parameters, a semiempirical absorption correction[12] was applied ($T = 0.552^{-1}.000$). In the final cycles of full-matrix least squares on F^2 all non-hydrogen atoms were assigned anisotropic thermal parameters and refinement converged at $R = 0.084$. Residual electron density is in the range +0.635 to −0.621 e $Å^{-3}$. All calculations were carried out on a PC 486 using the SHELXTL/PC program package.[13] Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[14]

Results and Discussion

The substituted pyrazole dithiocarboates were synthesized as their potassium salts by introducing the dithiocarboate group on the amines following a modified Trofimenko[7] route. Reaction of $NiCl_2 \cdot 6H_2O$ with KL^n [$n = 1-4$] in a 1:2 molar ratio in aqueous media and in air and at room temperature affords red-brown $Ni(L^n)_2$ ($n = 1-4$) in decent yield. All the complexes are insoluble in water and precipitate immediately. The complexes are soluble in dichloromethane, DMF, and DMSO where they display the expected electroneutrality.

The infrared spectra of the mononuclear complexes, $Ni(L^n)_2$ are characteristic in establishing the NiN_2S_2 chelation compared to NiS_4. The pyrazole ring vibration for all the complexes occurs in the range 1525−1580 cm^{-1}, which is lower than that of the free ligand value.[2a,3a,5a] The bands in the 1324−1349 cm^{-1} region are assignable to the C═S stretching expected for a N,S coordination mode.[15] The IR spectra of the complexes do not show any band assignable to the $\nu(CS_2)$ vibration modes[16] (in the 1150−1250 cm^{-1} region) expected for a S,S coordination of the pyrazolecabodithioate ligand. The $\nu_{C=S}$ band at 844−886 cm^{-1} remains unshifted indicating noncoordination of the >C═S end of the ligands. The N,S coordination mode of 3,5-dimethylpyrazole-1-carbodithioate as opposed to the S,S mode has been confirmed earlier by an X-ray crystal structure analysis of [$Cu(L^1)(CNR)_2$].[17] Electronic spectra of the $Ni(L^n)_2$ ($n = 1-4$) complexes in dichloromethane and dimethylformamide solutions show several intense absorptions in the visible region which are probably due to allowed ligand-to-metal charge-transfer transitions. The complexes all exhibit typical bands in the 500−200 nm region with high molar extinction coefficients (ϵ), indicating their charge-transfer nature (S → Ni). The bands are of similar type to that for other $Ni^{II}N_2S_2$ complexes.[5a,b,d,18]

Cyclic voltammogram of the $Ni(L^1)_2$ complex was recorded in dimethylformamide solution at a platinum electrode. An initial cathodic scan reveals a well-defined cathodic peak (E_{pc}) at −0.79 V and the corresponding anodic peak (E_{pa}) at −0.65 V vs SCE on scan reversal. At a scan rate of 50 mV s^{-1} the cathodic and anodic peak potential separation ΔE_p is 140 mV, suggesting a quasireversible one-electron process.[10a] The one-electron nature of this reduction was verified by the current height of the cyclic voltammogram and constant-potential coulometry and was assigned to a Ni(II)−Ni(I) reduction. On the positive side of the SCE an irreversible oxidative response is observed at +0.73 V. The second response is irreversible in nature and is tentatively assigned to Ni(II)−Ni(III) oxidation. The one-electron nature of this oxidation was established by comparing its current height (i_{pa}) with that of the Ni(I)−Ni(II) couple.

When $Ni(L^1)_2$ is dissolved in dichloromethane and layered with equal volume of *n*-hexane, red-brown shiny crystals of the dimer separated from a red-brown solution. The product corresponds to a dimeric nickel(II) complex of pyrazolecarbodithioate ligands and bridging pyrazolate anions formed by removal of two carbon disulfide molecules from two anionic L^1. This has been confirmed by X-ray crystallography, which revealed the dinickel(II/II) complex, [$Ni_2(\mu$-3,5-$Me_2Pz)_2(L^1)_2$], featuring the doubly bridged near square-planar coordination geometry as illustrated in Figure 1. Selected bond distances and angles are listed in Table 2. The pyrazolate bridge formation reaction (Scheme 1) following CS_2 elimination is similar to the well-documented thiolate bridge formation from thioxanthates.[4] What makes $Ni^{II}(L^1)_2$ (L^1 = 3,5-dimethylpyrazole-1-carbodithioate) noteworthy is that, unlike $Ni^{II}(dtc)_2$,[5] where the integrity of the ligand has been retained, $Ni^{II}(L^1)_2$ undergoes a facile and spontaneous transformation in solution affording the new dimer [$Ni_2(\mu$-3,5-$Me_2Pz)_2(L^1)_2$], incorporating pyrazoledithiocarboate chelation. This reaction provides a new way of generating

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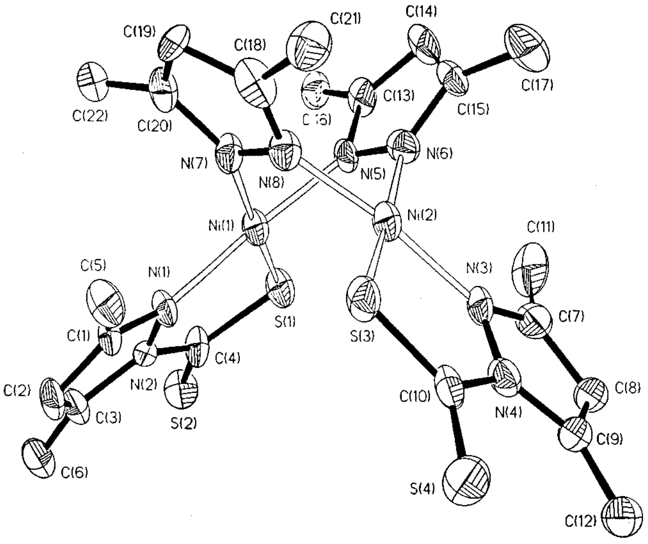
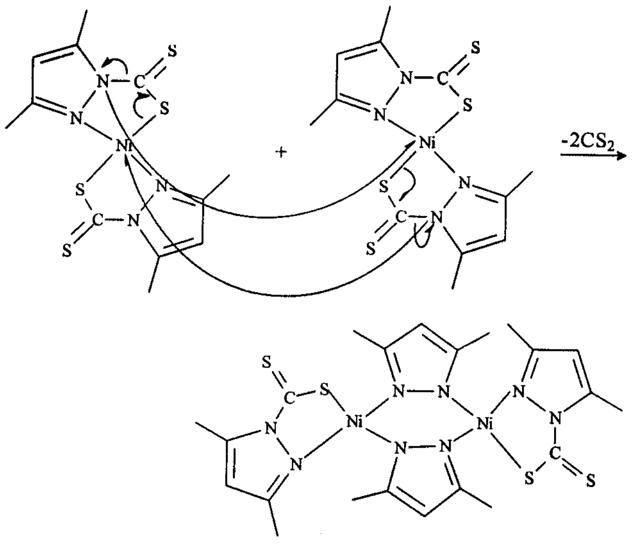


Figure 1. ORTEP of $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$ molecule showing 50% thermal probability ellipsoids and atom numbering scheme.

Table 2. Selected Bond Distances and Bond Angles for $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$

Bond Distances (Å)			
Ni (1)−N (5)	1.883 (4)	Ni (2)−N (6)	1.912 (4)
Ni (1)−N (7)	1.902 (4)	Ni (2)−N (8)	1.870(4)
Ni (1)−N (1)	1.898 (4)	Ni (2)−N (3)	1.879 (4)
Ni (1)−S (1)	2.138 (2)	Ni (2)−S (3)	2.121 (2)
S (1)−C (4)	1.724 (5)	S (3)−C (10)	1.690 (5)
S (2)−C (4)	1.612 (5)	S (4)−C (10)	1.644 (6)
N (1)−C (1)	1.300 (6)	N (3)−C (7)	1.350 (6)
N (1)−N (2)	1.421 (5)	N (3)−N (4)	1.379 (5)
Bond Angles (deg)			
N (5)−Ni (1)−N (1)	175.5 (2)	N (5)−Ni (1)−N (7)	85.6 (2)
N (1)−Ni (1)−N (7)	97.3 (2)	N (5)−Ni (1)−S (1)	90.78(11)
N (1)−Ni (1)−S (1)	86.73 (11)	N (7)−Ni (1)−S (1)	172.59 (14)
N (8)−Ni (2)−N (3)	171.9 (2)	N (8)−Ni (2)−N (6)	86.1 (2)
N (3)−Ni (2)−N (6)	98.8 (2)	N (8)−Ni (2)−S (3)	89.14(13)
N (3)−Ni (2)−S (3)	86.49 (12)	N (6)−Ni (2)−S (3)	173.04 (12)

Scheme 1



doubly pyrazole-bridged complexes. The structurally characterized N,S coordination mode of the bidentate pyrazoledithiocarboate ligand is similar to that characterized earlier.[17] The donor atoms in the dimer are distinguished below as follows: N_t, terminally chelated pyrazoledithiocarboate nitrogen; N_u, uncoordinated pyrazoledithiocarboate nitrogen; N_b, bridged pyrazolate nitrogen; S_t, terminally chelated dithiocarboate sulfur; S_u, uncoordinated dithiocarboate sulfur. In $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$, each metal is chelated by a pyrazoledithicarboate anion, forming a planar, five-membered $NiSCN_2$ ring. The bite angle of the anionic L^1 ligand lies close to 86.6°and is only slightly higher than those observed in either the same ligand in a mononuclear environment (82.6(2)°)[18] or in other N,S chelates (83.2−85.3°).[19] The two $Ni(L^1)$ moieties in the dinuclear molecule are linked by two pyrazolate bridges. The NiN_3S coordination environments are nearly perfectly planar. Indeed whole $[Ni(\mu\text{-}3,5\text{-}Me_2Pz)(L^1)]$ fragments are planar with a mean deviation of <0.079 Å. The dihedral angle between the two planes of this type is 75.8(2)°. The slightly distorted square-planar geometry results from coordination of the N_3S donor set which produces angles at the metal in the range 85.6(2)−98.8(2)°. The dithiocarboate sulfur donors [avg Ni − S, 2.130(2) Å] produce a substantially longer Ni−S bond length than either pyrazolate nitrogens [avg Ni−N, 1.891(4) Å]. A small but distinct tetrahedral distortion is observed only in the Ni(1) coordination sphere, where the trans donor pairs in S(1), N(7), and N(1), N(5), respectively, lie on opposite sides of the NiN_3S least-squares plane, although the maximum deviation from the plane is less than 0.095 Å. The $Ni-N_b$ distances average to 1.892(4) Å, which is slightly longer than the $Ni-N_t$ average [1.884(4) Å]. The nonbonded N(5)···N(7), N(6)···N(8), N(1)···S(3), and N(3)···S(1) contacts are, respectively, 2.571, 2.581, 4.881, and 4.930 Å. Similar bibridged homonuclear copper(II) and heteronuclear Ir−Co and Ru−Ni complexes have been reported in recent times.[20] The N−N distances[N(5)−N(6), 1.383(5) Å, N(7)−N(8), 1.356(5) Å] are shorter compared to other 3,5-dimethylpyrazolate-bridged nickel(I) dimer [1.463(4) Å] with $p\pi$-$d\pi$ interaction between the pyrazolyl π system and filled d orbitals on Ni.[21]

The reaction of dimeric $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$ complex with excess CS_2 in dichloromethane solution cannot regenerate the parent bis complex $[Ni(L^1)_2]$. Thus the transformation from the mononuclear bis complexes to the pyrazolate-bibridged dinickel complex is irreversible.[22] The possibility of using two bis/tris complexes as precursors for making heterobimetallic complexes, such as of Fe−Ni, utilizing the reported transformation of the pyrazoledithiocarboate ligands is currently under investigation.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $[Ni_2(\mu\text{-}3,5\text{-}Me_2Pz)_2(L^1)_2]$. This material is availble free of charge via the Internet at http://pubs.acs.org.

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