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Articles

Deprotonated Thioamides as Thiolate S-Donor Ligands with a High Tendency to Avoid M–S–M Bridge Formation: Crystal and Molecular Structure of [Ni(tmtssA)]$_2$

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The crystal structure of [Ni(tmtssA)]$_2$ (**1a**) (tmtssA = 2-hydroxy-5-methylacetophenone *N,N*-dimethylthiosemicarbazonato) is surprising in having a phenolate O-bridge rather than the expected imino thiolate S-bridge. This implies that deprotonated thioamides such as tmtssA, which bind in the imino thiolate form, have a much lower bridging tendency than alkane- or arenethiolates. Reasons are suggested as to why imino thiolates avoid several limitations of thiolates as ligands: bridge formation, C–S bond cleavage, and reduction of the metal. By analogy with the recognized basicity difference of syn and anti lone pairs in carboxylates, we suggest that the bridge-avoiding tendency of an imino thiolate is related to the low basicity of the S lone pair anti to the C=N group which would bind to the second metal in any dimer. Crystal data for [Ni(C$_{12}$H$_{15}$N$_3$OS)]$_2$ (**1a**): triclinic, space group $P\bar{1}$, a = 8.220(2) Å, b = 13.100(3) Å, c = 13.864(3) Å, α = 114.56(3)°, β = 103.59(3)°, γ = 92.07(3)°, Z = 2, R = 4.26% (3637 observed reflections).

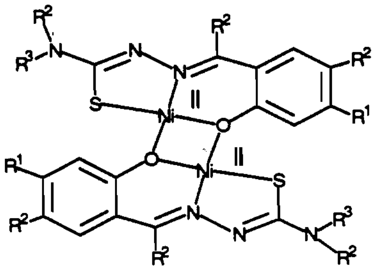
The very high tendency of thiolate groups to form M(μ-SR)$_2$M bridges is a factor that has retarded the study of coordination and organometallic chemistry in thiolate and related S-donor environments.[1] The formation of such species is especially common for nickel: [Ni(SEt)$_2$]$_6$ is a typical example.[2] Two additional limitations[1] of thiolates are their tendencies to undergo C–S bond cleavage and to reduce the metal by elimination of the disulfide RSSR. Using very hindered arenethiolates, such as the ones studied by Millar and Koch,[3] is one useful strategy for avoiding these limitations. We now find that deprotonated thioamides, which bind in the imino thiolate form (RN=CR—S$^-$), have a low bridging tendency. In addition, they can easily be incorporated into a multidentate chelate ligand.

In functional modeling of certain Ni enzymes,[4] we previously found catalytic activity for Ni(II) in an N,O,S-ligand environment, but only when the S-donor was an imino thiolate. For example, **1a** and **1b** catalyze eq 1, a key reaction of CO dehydrogenase,[5a] and **1c** catalyzes silane alcoholysis (eq 2), which is a related electrophilic activation of a small molecule.[5b] We wanted to know what makes the imino thiolate complexes catalytically active.

$$CO + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \qquad (1)$$

$$R_3SiH + R'OH \rightarrow R_3SiOR' + H_2 \qquad (2)$$

The catalyst **1a** has proved suitable for an X-ray crystallographic study. The resulting structure (Figure 1) shows that the compound is bridged not via S, as we expected, but via the phenolate O. The phenolate bridge is weak, as shown by the ease of bridge splitting. This implies that thioamide S has a low tendency to bridge and helps explain the catalytic activity. Only if the bridge bonding is sufficiently weak, will the substrate CO be able to bind to nickel, assuming a 4-coordinate product. The related complex [Cu(tss)]$_2$ (tss = thiosemicarbazidosalicylaldiminato) was said[6] to be O-bridged on the basis of a crystal structure, but no details were reported.



1a, (R^1 = H, R^2 = R^3 = Me)
1b, (R^1 = R^2 = Me, R^3 = H)
1c, (R^1 = R^2 = R^3 = H)

Results

The ligands tmtssAH$_2$ were prepared in good yield as white crystals by condensing the appropriately substituted acetophenones with the appropriate semicarbazides in MeOH. The complexes were prepared in excellent yield as brown powders or as dark red crystals from the ligand and Ni(OAc)$_2$ in refluxing MeOH, the acetate being the base that deprotonates the ligand.

Both **1a** and **1b** gave normal ^{1}H NMR spectra in CDCl$_3$ (**1a**) or DMSO (**1b**) solution, consistent with the presence of diamagnetic square planar Ni(II). The expected ligand resonances

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(1) Müller, A.; Diemann, E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Chapter 16.1.

(2) Woodward, P.; Dahl, L. F.; Abel, E. W.; Crosse, B. C. *J. Am. Chem. Soc.* **1965**, *87*, 5251.

(3) Gebhard, M. S.; Deaton, J. C.; Koch, S. A.; Millar, M.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 2217.

(4) Lancaster, J. R. *The Bioinorganic Chemistry of Nickel*; VCH: Weinheim, Germany, 1986.

(5) (a) Lu, Z.; White, C.; Rheingold, A.; Crabtree, R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 92. (b) Barber, D.; Lu, Z.; Richardson, T.; Crabtree, R. *Inorg. Chem.* **1992**, *31*, 4709.

(6) Revenko, M. D.; Gerbeleu, N. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1972**, *17*, 529.

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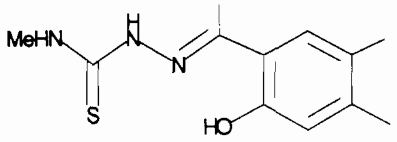
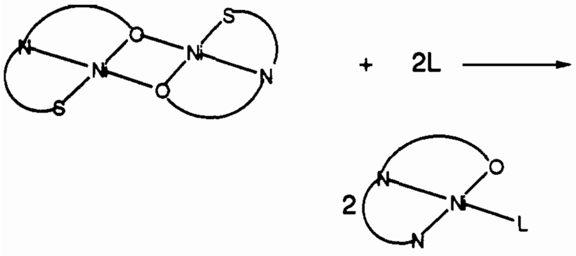


tmtssAH 2

are seen; for example, in **1a** the aromatic protons appear at 6.8–7.2 ppm and the four methyl groups appear as singlets in the range 2.1–3.1 ppm.

The complexes formed mononuclear adducts with a variety of monodentate ligands, such as pyridine, DMSO, H_2O,[7] RNC, and CN^-. These are formed by splitting the O-bridge as shown in eq 3. The first three species are of a known type;[7] only the isonitrile and cyanide are new. Na[Ni(tmtss)CN] (**3**) has ν(CN) = 2118 cm^{-1}, appropriate for a terminal cyanide.[8]



(3)

Crystals of **1a**, obtained from CH_2Cl_2/Et_2O, were suitable for an X-ray structural study (Figure 1). Table I gives the crystal data, Table II, the positional data, and Table III, selected bond lengths and angles. Other data appear as supplementary material. The molecule is a dimer bridged by the phenolate oxygen. Each half of the dimer is a square planar Ni(II) complex with three ligands provided by the tmtss ligand and the fourth by a phenolate from the other half. There are no unusual intermolecular contacts.

Discussion

This system allows us to compare the bridging tendencies of phenolate and imino thiolate ligands. Surprisingly, the O-donor ligand prefers to bridge. The bridge bonding is relatively weak as shown by the easy splitting of the bridge with various ligands including CN^-. The resulting cyanide, which is relevant to the catalytic reaction because CN^- is isoelectronic with CO, is monomeric by X-ray crystallography.[8b] Binding of CO to Ni(II) is rare but not unknown.[8c]

A reviewer has suggested the possibility that the dimer is O-bridged because the Ni prefers O to S on ligand field grounds. To test this, we have now studied the analogues of [Ni(tmtss)] in which the thiosemicarbazide fragment has been replaced by both aromatic and aliphatic thiolates, using the Schiff bases from o-$C_6H_4(NH_2)SH$ or $H_2NCH_2CH_2SH$ and salicylaldehyde as the ligands. Both of these complexes are S-bridged by X-ray crystallography, are catalytically inactive, and resist bridge-splitting reactions with H_2O. The aromatic compound is a tetramer and the aliphatic one a trimer.[8d]

The structure shows no counterions, which implies that the $tmtssH_2$ ligand is doubly deprotonated in the complex. This is accompanied by tautomerization of the ligand to the imino thiolate form. The bond lengths for **1a** confirm this picture: the C–S bonds (1.736 and 1.744 Å) are essentially single bonds, and C(8)–N(2) (1.298 Å) and C(20)–N(5) (1.317 Å) have bond orders closer to 2 than to 1. The reduction in the bond order from 2 may be a result of conjugation between the carbazone C=N double bond and the adjacent N=N bond. The ligand therefore binds as an imino thiolate as shown in **2**.

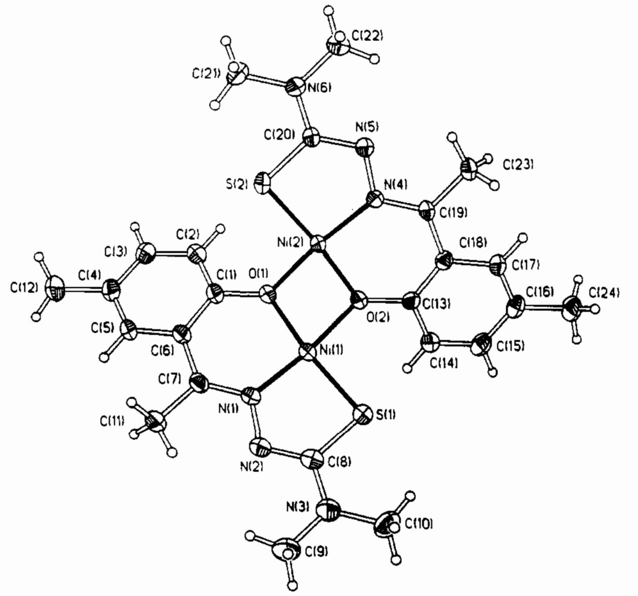


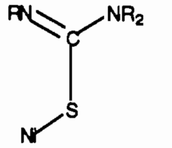
Figure 1. ORTEP drawing of $[Ni(C_{12}H_{15}N_3OS)]_2$ (**1a**) with numbering scheme and vibrational ellipsoids at the 50% probability level.

Table I. Crystallographic Data for $[Ni(C_{12}H_{15}N_3OS)]_2$ (**1a**)

empirical formula: $C_{24}H_{30}N_6Ni_2O_2S_2$
fw = 616.1
a = 8.220(2) Å
b = 13.100(3) Å
c = 13.864(3) Å
α = 114.56(3)°
β = 103.59(3)°
γ = 92.07(3)°

space group: $P\bar{1}$ (No. 2)
Z = 2
V = 1304.6(7) Å^3
t = 25 °C
$R(F)^a$ = 0.0426
$R_w(F)^b$ = 0.0567
λ(Mo Kα) = 0.710 73 Å
D_{calcd} = 1.568 g/cm^3
μ = 16.37 cm^{-1}

^{a} $R(F) = \omega(F_o - F_c)/\Sigma F_o$. ^{b} $R_w(F) = [\Sigma w(F_o - F_c)^2/\Sigma(wF_o^2)]^{1/2}$. $w = [\sigma^2(F) + 0.0002F^2]^{-1}$.



2

Thiourea and its analogues are well recognized as S-donor ligands,[9] but they are not normally deprotonated. Thiosemicarbazide derivatives, on the other hand, can be found both protonated[10a] and deprotonated.[10b] In our system, deprotonation takes place at the hydrazine, not the amino, NH group. This is probably preferred because it allows the N=N double bond to be conjugated with the adjacent C=N double bond.

We suggest a rationalization of the bridge-avoiding tendency of these ligands on the basis of an analogy between imino thiolate and carboxylate. As shown in **3**, the syn lone pair of a carboxylate is known[11] to be much more basic than the anti lone pair ($K_{syn}/K_{anti} > 10^4$). Dipole–dipole repulsion between the C=O group dipole and the syn O lone pair is thought to destabilize this lone pair and make it more basic. If so, exactly the same mechanism

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[7] Ablov, A. V.; Gerbeleu, N. V. *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **1965**, *10*, 624.

[8] (a) Sato, M.; Sato, F.; Yoshida, T. *J. Organomet. Chem.* **1971**, *31*, 415. (b) Lu, Z.; Crabtree, R. H. *Inorg. Chim. Acta*, in press. (c) Saint-Joly, C.; Mari, A.; Gleizes, A.; Dartiguenave, M.; Dartiguenave, Y.; Galy, J. *Inorg. Chem.* **1980**, *19*, 2403. (d) Lu, Z.; Rheingold, A. L.; Crabtree, R. H. *Inorg. Chem.*, in press.

[9] Livingstone, S. E. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, U.K., 1987; Chapter 16.6.

[10] (a) Gronbeck-Hazell, R. *Acta Chem. Scand.* **1972**, *26*, 1365. (b) Carvalca, L.; Nardelli, M.; Fava, G. *Actra Crystallogr.* **1962**, *15*, 1139.

[11] Wang, X.; Houk, N. *J. Am. Chem. Soc.* **1988**, *110*, 1870. Gandour, R. D. *Bioorg. Chem.* **1981**, *10*, 169.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters for **1a**

	x	*y*	*z*	*U*,[a] Å^2
Ni(1)	2893(1)	5940(1)	8939(1)	36(1)
Ni(2)	948(1)	6507(1)	7403(1)	36(1)
S(1)	4576(2)	7003(1)	10513(1)	45(1)
S(2)	−1668(2)	5965(1)	6563(1)	51(1)
O(1)	1418(4)	5160(2)	7543(3)	48(1)
O(2)	3192(4)	6874(3)	8221(3)	46(1)
N(1)	2294(4)	4974(3)	9511(3)	36(1)
N(2)	2959(5)	5263(3)	10631(3)	43(2)
N(3)	4859(6)	6515(3)	12230(3)	57(2)
N(4)	737(4)	7910(3)	7389(3)	32(1)
N(5)	−842(4)	8134(3)	6953(3)	38(1)
N(6)	−3634(4)	7381(3)	6105(3)	49(2)
C(1)	572(6)	4088(3)	7102(4)	40(2)
C(2)	−74(6)	3540(4)	5959(4)	49(2)
C(3)	−882(6)	2435(4)	5453(4)	53(2)
C(4)	−1079(6)	1860(4)	6072(4)	52(2)
C(5)	−411(6)	2409(4)	7195(4)	46(2)
C(6)	455(5)	3538(3)	7762(4)	38(2)
C(7)	1193(5)	4024(3)	8959(3)	37(2)
C(8)	4050(6)	6188(4)	11151(4)	42(2)
C(9)	4402(8)	5874(5)	12789(4)	71(3)
C(10)	5865(7)	7630(4)	12927(4)	64(2)
C(11)	719(6)	3395(4)	9564(4)	48(2)
C(12)	−1986(8)	643(4)	5517(5)	71(3)
C(13)	4281(5)	7792(3)	8480(3)	37(2)
C(14)	5993(5)	7764(4)	8867(4)	42(2)
C(15)	7187(6)	8668(4)	9115(4)	48(2)
C(16)	6705(5)	9620(4)	8998(4)	43(2)
C(17)	5006(5)	9634(3)	8586(3)	38(2)
C(18)	3740(5)	8712(3)	8297(3)	32(2)
C(19)	1968(5)	8771(3)	7797(3)	33(2)
C(20)	−2045(5)	7258(3)	6557(3)	37(2)
C(21)	−5095(6)	6547(4)	5820(4)	51(2)
C(22)	−3930(7)	8416(4)	6011(4)	58(2)
C(23)	1581(6)	9865(4)	7744(4)	47(2)
C(24)	8015(6)	10616(4)	9270(5)	60(3)

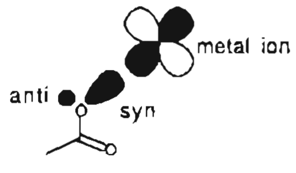
[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Selected Bond Lengths (Å) and Angles (deg) for **1a**

	Bond Lengths		
Ni(1)–Ni(2)[a]	2.729(1)	Ni(1)–S(1)	2.129(1)
Ni(1)–O(1)	1.851(3)	Ni(1)–O(2)	1.912(4)
Ni(1)–N(1)	1.855(5)	Ni(2)–S(2)	2.123(1)
Ni(2)–O(1)	1.898(4)	Ni(2)–O(2)	1.850(3)
Ni(2)–N(4)	1.860(4)	S(1)–C(8)	1.744(6)
S(2)–C(20)	1.736(5)	O(1)–C(1)	1.358(5)
O(2)–C(13)	1.337(5)	N(1)–N(2)	1.397(5)
N(1)–C(7)	1.325(5)	N(2)–C(8)	1.298(5)
N(4)–C(19)	1.317(5)	N(4)–N(5)	1.394(5)
N(5)–C(20)	1.317(5)		
	Bond Angles		
S(1)–Ni(1)–O(1)	173.5(1)	O(1)–Ni(1)–O(2)	76.4(1)
S(1)–Ni(1)–O(2)	97.6(1)	S(1)–Ni(1)–N(1)	89.2(1)
O(1)–Ni(1)–N(1)	96.6(2)	O(2)–Ni(1)–N(1)	172.0(1)
S(2)–Ni(2)–O(1)	97.5(1)	O(1)–Ni(2)–O(2)	76.8(1)
S(2)–Ni(2)–O(2)	173.1(1)	S(2)–Ni(2)–N(4)	89.2(1)
O(1)–Ni(2)–N(4)	173.1(1)	O(2)–Ni(2)–N(4)	96.4(1)
Ni(1)–S(1)–C(8)	94.8(1)	Ni(2)–S(2)–C(20)	95.1(1)
Ni(1)–O(1)–Ni(2)	93.4(1)	Ni(1)–O(1)–C(1)	126.5(3)
Ni(2)–O(1)–C(1)	134.8(3)	Ni(1)–O(2)–Ni(2)	93.0(2)
Ni(1)–O(2)–C(13)	134.4(3)	Ni(2)–O(2)–C(13)	127.6(3)
Ni(1)–N(1)–N(2)	119.7(3)	Ni(1)–N(1)–C(7)	125.8(3)
N(2)–N(1)–C(7)	114.4(4)	N(1)–N(2)–C(8)	113.3(5)
Ni(2)–N(4)–C(19)	125.8(3)	Ni(2)–N(4)–N(5)	120.0(3)
N(4)–N(5)–C(20)	112.7(4)	N(5)–N(4)–C(19)	114.2(4)
S(1)–C(8)–N(2)	122.9(4)	S(2)–C(20)–N(5)	122.9(3)

[a] Nonbonding distance.

should apply in our deprotonated imino thiolate group, **4**. The observed deprotonation at the endocyclic hydrazide NH rather than at the exocyclic amino NH_2 directs the more basic of the two S sp^2 lone pairs toward the metal. This in turn directs the less basic lone pair toward the position that any second metal would have to occupy in a bridged system. Bridging is therefore disfavored. These arguments explain why alkanethiolate analogues of **1** often form[12] strong bridges with a folded Ni_2S_2 ring. We have searched the Cambridge Crystallographic Database to document these structural preferences in M_nS_n bridges.[8d]



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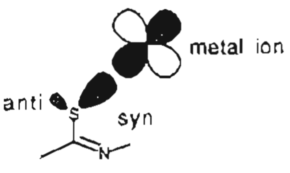

4

The halves of **1a** are folded relative to one another with a dihedral angle of 135.0(1)°. This is probably in part the result of steric interference in the coplanar form but presumably also reflects an sp^3 hybridization at O. The bridged Ni–O bond lengths of 1.898(4) and 1.912(4) Å are longer than the Ni–O distances within the Ni(tmtss) fragment itself (1.850(3) and 1.851(3) Å). The folding and the long bridge bonds are indications of the weak bridging in the system.

Using imino thiolates as S-donors also seems to avoid two additional limitations associated with thiolates:[1] their tendencies (i) to undergo C–S bond cleavage and (ii) to reduce the metal by elimination of the disulfide RSSR. C–S cleavage seems often to be homolytic, and so the fact that vinyl (and phenyl) radicals are very unstable relative to their alkyl and especially 3° alkyl analogues may explain the cleavage resistance of imino thiolates and arenethiols. In contrast to alkane- and arenethiols, the disulfide form of a thioamide does not seem to be stable and so reduction of the metal is strongly disfavored.

Conclusion

Thiolates and imino thiolates show very different bridging abilities. Our working hypothesis is that an alkanethiolate can use its more basic sp^3 lone pair to bridge, as is suggested by the fact that the Ni_2S_2-bridged system is often strongly folded.[8d,12] A lower basicity for imino thiolate S is consistent with rehybridizing the lone pairs from sp^3 to $p + sp^2$, where the sp^2 lone pair is available for binding the metal and the p lone pair is delocalized with the adjacent C=N double bond. Dipole–dipole effects cause the sp^2 lone pairs to have different basicities, which can further disfavor bridging.

Experimental Section

All the chemicals were obtained from Aldrich and used without further purification. Thiosemicarbazidosalicylaldimine ($tssH_2$) and complex **1c** were prepared as reported previously.[6]

2-Hydroxy-5-methylacetophenone *N,N*-Dimethylthiosemicarbazone ($tmtssH_2A$). 2-Hydroxy-5-Methylacetophenone (1.50 g, 0.01 mol) readily condensed with *N,N*-dimethyl-3-thiosemicarbazide (1.19 g, 0.01 mol) in ethanol (25 mL). Yield: 65%. Anal. Calcd for $C_{12}H_{17}N_3OS$ (fw 251.35): C, 57.33; H, 6.82; N, 16.72. Found: C, 57.36; H, 6.86; N, 16.74. ^1H NMR (250 MHz, $CDCl_3$): δ 11.91 (s, 1H, OH), 8.22 (s, 1H, NH), 7.13 (s, 1H, C_6H_3), 7.07 (d, 1H, C_6H_3), 6.88 (d, 1H, C_6H_3), 3.32 (s, 6H, $2CH_3$), 2.26 (s, 6H, $2CH_3$).

2-Hydroxy-4,5-dimethylacetophenone *N*-methylthiosemicarbazone ($tmtssH_2B$) was prepared similarly. Yield: 69%. Anal. Found: C, 57.22; H, 6.72; N, 16.63. ^1H NMR (250 MHz, $CDCl_3$): δ 10.50 (s, 1H, OH), 8.59 (s, 1H, NH), 7.18 (s, 1H, C_6H_2), 6.78 (s, 2H, NH, C_6H_2), 3.25 (d, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.21 (s, 3H, CH_3).

Bis[(2-hydroxy-5-methylacetophenone *N,N*-dimethylthiosemicarbazonato)nickel(II)], $[Ni(tmtssA)]_2$ (1a). To a stirred suspension of $tmtssH_2$ (0.500 g, 2 mmol) in ethanol (20 mL) was slowly added ethanolic (20 mL) nickel acetate (0.496 g, 2 mmol). After 2-h reflux, a brownish precipitate was filtered off, washed with cold ethanol, and dried in vacuo. Yield: 0.561 g, 91%. Anal. Calcd for $C_{24}H_{30}N_6O_2S_2Ni_2$ (fw 616.06):

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[12] Baidya, N.; Olmstead, M. M.; Mascharak, P. K. *Inorg. Chem.* **1989**, *28*, 3426. Fackler, J. P. *Prog. Inorg. Chem.* **1976**, *21*, 550.

C, 46.79; H, 4.91; N, 13.64. Found: C, 46.79; H, 4.96; N, 13.57. The complex can be recrystallized from CH_2Cl_2/Et_2O. ^1H NMR (250 MHz, $CDCl_3$): δ 7.11 (s, 1H, C_6H_3), 6.94 (d, 1H, C_6H_3), 6.88 (d, 1H, C_6H_3), 3.01 (s, 6H, $2CH_3$), 2.43 (s, 3H, CH_3), 2.19 (s, 3H, CH_3).

Bis[(2-hydroxy-4,5-dimethylacetophenone *N*-methylthiosemicarbazonato)nickel(II)], [Ni(tmtssB)]$_2$ (1b), was prepared similarly. Yield: 0.549 g, 89%. Anal. Found: C, 47.0; H, 4.87; N, 13.5. ^1H NMR (250 MHz, DMSO): δ 7.21 (s, 1H, C_6H_2), 6.55 (s, 2H, NH, C_6H_2), 2.59 (d, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.07 (s, 3H, CH_3).

Crystallographic Measurement. Single crystals of [Ni(tmtssA)]$_2$ (**1a**) were obtained by slow diffusion of Et_2O into a solution of the complex in CH_2Cl_2; crystal size 0.18 × 0.34 × 0.38 mm. Data collection was performed at 298 K on a Siemens R3m/V diffractometer with Mo Kα radiation (λ = 0.710 73 Å, range $4.0 < 2\theta < 54.0°$, variable scan speed 5.00–20.00°/min, scan range 1.00°). A total of 5702 independent reflections were collected, of which 3637 were considered observed with $F > 5.0\sigma(F)$. No absorption correction was applied. Structure solution was accomplished via the Patterson synthesis using the Siemens SHELXTL Plus program system. A full-matrix least-squares refinement was carried out on F using the same program system. The final cycle of refinement included 325 independent parameters and converged with $R = 0.0426$, $R_w = 0.0567$. H atoms were included at calculated positions by using a fixed isotropic U value of 0.080 Å^2. All non-hydrogen atoms were refined with anisotropic thermal parameters. The weighting scheme used was $w^{-1} = (\sigma^2(F) + 0.0020F^2)$. Largest Δ/σ = 0.001, largest difference peak = 0.71 e Å^{-3}, and largest difference hole = –0.51 e Å^{-3}.

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Supplementary Material Available: Full tables of data collection parameters, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters for [Ni(tmtssA)]$_2$ (**1a**) (7 pages). Ordering information is given on any current masthead page.