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Coordination Chemistry of New Sulfur-Containing Ligands. 22. Synthesis and Structure of Bis(pyridine)bis(pyrrole-*N*-carbothioato)nickel(II), $Ni(SOCNC_4H_4)_2(C_5H_5N)_2$. Evidence for New Resonance Forms in Monothiocarbamates[1]

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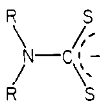
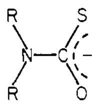
This bis(pyridine) adduct of the Ni(II) complex of pyrrole-*N*-carbothioate, $Ni(ptc)_2(py)_2$ has been synthesized by the addition of pyridine to a THF solution of $Ni_2(ptc)_4 \cdot 3THF$. The crystal and molecular structure of the title compound has been solved by a single-crystal X-ray diffraction study at room temperature. The compound crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 11.423$ (5) Å, $b = 9.415$ (4) Å, $c = 21.651$ (11) Å, $\beta = 112.92$ (3)°, $V = 2145$ (2) Å^3, and d_{obsd} (d_{calcd}) = 1.46 (1.45) g/cm^3 for a mol wt = 469.2 and $Z = 4$. Diffraction data were collected with a Syntex $P\bar{1}$ diffractometer using Mo Kα radiation ($\lambda = 0.71069$ Å). The nickel atom was located from a Patterson synthesis, and all other nonhydrogen atoms were located via difference Fourier techniques. Hydrogens were placed in calculated positions whenever necessary. Least-squares refinement resulted in $R_F = 6.9\%$ and "goodness-of-fit" = 1.28 for all 1469 reflections having $I \geq 3\sigma(I)$ with $5° < 2\theta < 42°$. The molecules are well separated and monomeric. The coordination geometry about the Ni atom is best described as a distorted octahedron. The arrangement of the nitrogen, sulfur, and oxygen donor atoms is discussed in terms of the trans influence. In addition, bond distances and angles indicate little or no contribution from the resonance form usually associated with monothiocarbamates. Comparisons between this new (aromatic) monothiocarbamate and dialkylmonothiocarbamates are made.

Introduction

In contrast to the great deal of attention which has been focused on the coordination chemistry and reactivity of dithiocarbamate (dtc) complexes in recent years,[2] only a very modest amount of work has appeared on similar studies of monothiocarbamates (mtc). For example only ten structures of monothiocarbamate complexes with transition metals have been reported. These include $Fe(Me_2mtc)_3$,[3] $Co(pyrmtc)_2 \cdot 2pyr$ (pyr = pyrrolidine),[4] $[Ni(n\text{-}Bu_2mtc)_2]_6$,[5] $[Cu(n\text{-}Pr_2mtc)_6$,[6] $[Ag(n\text{-}Pr_2mtc)]_6$,[7] $Zn(pipmtc)_2 \cdot 2pip$ (pip = piperdine),[8] $M(Et_2mtc)_4$[9] (M = Ti, Zr), $Ti(Et_2mtc)_3Cl$,[10] and $UO_2(n\text{-}Pr_2mtc)_2(OEt)$.[11] In part due to the larger number of resonance structures which are possible for monothiocarbamates (eq 1) than for dithiocarbamates (eq 2), a much more varied coordination chemistry is expected in these complexes. This is clearly evident in the variety of structures which have been reported to date. Results from earlier studies have suggested that resonance form IC predominates in monothiocarbamates. As a result, the sulfur atom has considerable "mercaptide" character and polymeric inorganic compounds are common.[5,12,13] To date, the primary concern in monothiocarbamate chemistry has been to determine if different reactivities and structures exist than found for similar dithiocarbamate systems. In an attempt to alter the reactivity within the monothiocarbamate ligand class, we have attempted to affect the bonding properties of the COS moiety by altering the peripheral ligand structure. It has been shown that a very different kind of dithiocarbamate[14] or dithioacid ligand[15] could be produced by choosing R groups which would strongly favor one of the possible resonance structures. In particular, the pyrroledithiocarbamate has been shown to essentially possess resonance form IIA while the properties of other dithiocarbamates are dominated by form IIB.[14]


R_2dtc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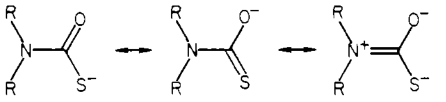
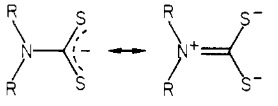


(1)

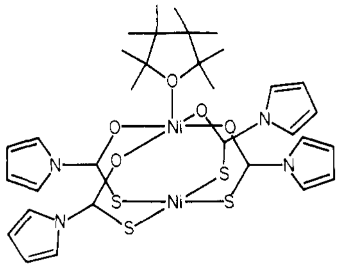
IA IB IC



(2)

IIA IIB

Recent work in our laboratories has shown that the pyrrole-*N*-carbothioate (ptc) ligand does indeed yield coordination compounds of different stoichiometries than dialkylmonothiocarbamates. For example, $[(R_2mtc)_2Ni]_6$ is hexameric[16] while the reaction of ptc with Ni(II) results in a dimer whose structure has been *suggested* based on magnetic studies.



We report here the preparation and X-ray structure of the

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[1] Part 21: Bereman, R. D.; Baird, D. M.; Hatfield, W. E. *J. Inorg. Nucl. Chem.* **1982**, *43*, 2729–33.

[2] (a) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 294–371. (b) Coucouvanis, D. *Ibid.* **1979**, *26*, 301–469. (c) burns, R. P.; McCullough, F. P.; McAuliffe, G. A. *Adv. Inorg. Chem. Radiochem.* **1980**, *23*, 211–69.

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Table I. Physical Data and Data Collection Parameters

mol formula	$C_{20}H_{18}NiN_4O_2S_2$
mol wt	469.2
crystal size, mm	0.08 × 0.12 × 0.08
cell dimens	
a, Å	11.423 (5)
b, Å	9.415 (4)
c, Å	21.651 (11)
β, deg	112.92 (3)
V, Å³	2145 (2)
space group	$P2_1/c$
molecules/unit cell	4
d_{calcd}, g/cm³	1.45
d_{obsd},[a] g/cm³	1.46
scan technique	$\theta/2\theta$
scan speed, deg/min	2 (in 2θ)
scan width, deg	1.2 below $K\alpha_1$ to 1.2 above $K\alpha_2$
bkgd count time	0.6 × scan time on each side of peak
no. of reflctns	2670
no. of nonzero reflctns[b]	1469

[a] Density was measured by the flotation technique with hexane/1,3-dibromopropane. [b] All intensities with values less than 3× standard deviation were set equal to zero with zero weight.

monomeric compound $Ni(ptc)_2\cdot 2py$ (py = pyridine) where we are particularly concerned with bond distances within the ptc ligand, especially in the Ni(COS) chelate ring, and how these might relate to the proposed resonance structure(s) of this new monothiocarbamate.

Experimental Section

Synthesis. The synthesis and all manipulations of this compound were carried out with standard Schlenk techniques even though the compound shows only modest moisture or air sensitivity. THF was dried over and distilled from Na/benzophenone just prior to use. Pyridine and hexanes were stored over 4-Å molecular sieves.

Spectra. Infrared spectra were recorded with a Perkin-Elmer 521 spectrophotometer with the sample in anhydrous Nujol mulls supported on CsBr plates.

Elemental Analyses. Analyses were obtained from Atlantic Microlabs, Atlanta, GA.

$Ni(ptc)_2(py)_2$. $Ni_2(ptc)_4\cdot THF$[1] (1 g) was dissolved in 50 mL of dry THF, and 5 mL of dry pyridine was added slowly. The solution changed from yellow to emerald green over a 1-h period. Addition of anhydrous hexanes and refrigeration produced blue-green crystals which were isolated by filtration and dried with a slow stream of anhydrous Ar. Anal. Calcd for $C_{20}H_{18}N_4O_2S_2Ni$: C, 49.28; H, 4.13; S, 11.49. Found: 49.35; H, 4.18; S, 11.49.

Crystal Data Collection. Blue, prismatic crystals suitable for an X-ray analysis were grown by refrigeration of a THF/hexane solution of the compound. Crystals grew slowly over a 2-week period. The crystal survey, unit cell dimension determination, and data collection were accomplished on a Syntex P$\bar{1}$ diffractometer using molybdenum radiation (λ = 0.710 69 Å) at room temperature. The diffractometer was equipped with a graphite incident-beam monochromator mounted in the perpendicular mode. Final unit cell dimensions were obtained by a least-squares fit of 15 high-angle reflections ($2\theta > 15°$). Systematic absences indicated that the crystal belonged to the monoclinic space group $P2_1/c$ ($0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$). A 1-Å intensity data set was collected (maximum $(\sin\theta)|\lambda = 0.5$). One check reflection monitored every 30 reflections revealed no unexpected variation in intensity. Details of the crystal survey and data collection parameters are summarized in Table I.

The diffractometer output and all subsequent crystallographic calculations were processed with subprograms of the CRYM crystallographic computer system.[17] The data processing included corrections for background, Lorentz, and polarization effects. Polarization due to the monochromator was corrected for by a method suggested by Azaroff.[18] Processing also included the calculation of F^2 and its standard deviation for each reflection. The standard deviations were assigned on the basis of the equation $\sigma^2(I) = S + \alpha^2(B_1 + B_2) + (dS)^2$, where S is the number of counts collected during the scan, B_1 and B_2 are the background counts, d is an empirical constant set at 0.02, and α is the scan time to total background time ratio. As a result of the "equidimensional" nature of the crystal, and the low linear absorption coefficient ($\mu = 11.0$ cm^{-1}), no absorption corrections were made.

Table II. Nonhydrogen Atom Coordinates and Their Standard Deviations[a]

	x/*a*	*y*/*b*	*z*/*c*
Ni	1592 (1)	7706 (1)	3758 (1)
S1	455 (3)	8668 (3)	4405 (1)
S2	2090 (3)	9899 (3)	3276 (1)
O1	−352 (5)	8013 (6)	3148 (3)
O2	2104 (5)	7283 (7)	2959 (3)
C1	−648 (9)	8448 (10)	3604 (5)
C2	2220 (8)	8544 (11)	2805 (4)
C3	2689 (9)	7737 (12)	1843 (5)
C4	2858 (11)	8325 (14)	1316 (5)
C5	2766 (12)	9799 (14)	1406 (6)
C6	2516 (10)	10076 (11)	1946 (6)
C7	−2868 (10)	8723 (11)	2837 (5)
C8	−3976 (10)	8978 (14)	2884 (7)
C9	−2442 (10)	9096 (12)	3926 (6)
C10	−3724 (12)	9216 (13)	3569 (8)
C11	4252 (11)	6700 (12)	4328 (5)
C12	3850 (9)	8284 (12)	4991 (5)
C13	5095 (11)	8218 (15)	5456 (6)
C14	5923 (10)	7368 (16)	5341 (6)
C15	5518 (10)	6656 (16)	4764 (7)
C16	1182 (9)	5140 (11)	4455 (5)
C17	839 (9)	3774 (12)	4531 (5)
C18	580 (8)	2844 (11)	4013 (5)
C19	611 (9)	3286 (10)	3418 (5)
C20	910 (8)	4678 (11)	3370 (4)
N1	−1911 (7)	8775 (8)	3473 (4)
N2	2492 (7)	8773 (8)	2232 (4)
N3	3421 (7)	7527 (9)	4440 (4)
N4	1208 (6)	5606 (8)	3881 (4)

[a] The values have been multiplied by 10^4.

Finally, the data set was placed on an approximately absolute scale by Wilson statistics.[19] Atomic scattering factors for C, N, O, and S were taken from ref 20a, for Ni^{2+} from Cromer and Mann,[20b] and for H from Stewart, Davidson, and Simpson.[21] The scattering factors for S and Ni(II) were corrected for the real anomalous scattering component.[20b]

Determination and Refinement of Structure. The position of the nickel atom was determined from a three-dimensional Patterson synthesis. Subsequent difference Fourier maps allowed the location of all carbon, nitrogen, oxygen, and sulfur atoms. This trial structure refined routinely to an acceptable R index of 0.069.

The refinement was concluded with a full-matrix least-squares technique. The quantity minimized by the least-squares procedure was $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$. Hydrogen positions were calculated wherever required. While the hydrogen parameters were added to the structure factor calculations during the later stages of refinement, they were not refined. During the final cycles of refinement the scale factor, nonhydrogen coordinates, and nonhydrogen anisotropic temperature factors were located in a single matrix. Refinement of a secondary extinction coefficient proved that this correction was insignificant. The refinement was terminated when the shifts calculated for the parameters in the least-squares cycles were all zero. A final difference Fourier revealed no extraneous electron density. The data fit criteria (based on nonzero reflections) were

$$R = \sum||F_o| - |F_c||/\sum F_o = 0.069$$

$$R' = \sum w(F_o^2 - F_c^2)^2/\sum F_o^4 = 0.007$$

$$\mathrm{GOF} = [\sum w(F_o^2 - F_c^2)^2/(m - s)]^{1/2} = 1.28$$

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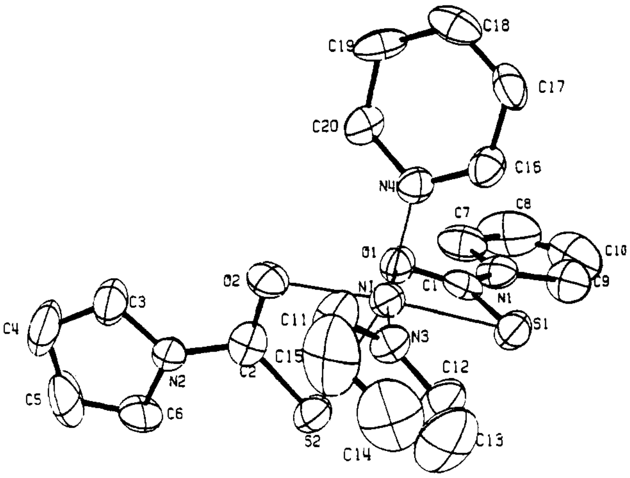


Figure 1. ORTEP of $NiL_2(py)_2$; 50% thermal ellipsoids

Table IV[a]

	Bond Distances within the Ligand		
S1–C1	1.713 (10)	C9–C10	1.369 (19)
S2–C2	1.675 (10)	C9–N1	1.372 (14)
O1–C1	1.231 (11)	C11–C15	1.386 (18)
O2–C2	1.254 (12)	C11–N3	1.322 (15)
C1–N1	1.392 (14)	C12–C13	1.388 (17)
C2–N2	1.409 (12)	C12–N3	1.310 (13)
C3–C4	1.348 (15)	C13–C14	1.334 (19)
C3–N2	1.364 (13)	C14–C15	1.330 (19)
C4–C5	1.412 (19)	C16–C17	1.372 (15)
C5–C6	1.332 (17)	C16–N4	1.329 (12)
C6–N2	1.380 (13)	C17–C18	1.360 (14)
C7–C8	1.330 (17)	C18–C19	1.368 (14)
C7–N1	1.387 (14)	C19–C20	1.369 (14)
C8–C10	1.414 (21)	C20–N4	1.345 (12)
	Bond Distances to Ni		
Ni–S1	2.426 (5)	Ni–O2	2.067 (4)
Ni–S2	2.476 (5)	Ni–N3	2.042 (4)
Ni–O1	2.115 (4)	Ni–N4	2.065 (4)

[a] Units: Å.

The refined coordinates were plotted with the ORTEP computer program of Johnson[22] (Figure 1). The final coordinates are given in Table II; thermal parameters are available in the supplementary materials (Table III).

Table V[a]

	Angles within Ligand		
O1–C1–S1	121.9 (8)	C14–C13–C12	119.4 (11)
N1–C1–S1	118.3 (7)	C15–C14–C13	117.7 (12)
N1–C1–O1	119.8 (8)	C14–C15–C11	121.0 (12)
O2–C2–S2	121.0 (7)	N4–C16–C17	122.2 (9)
N2–C2–S2	121.5 (8)	C18–C17–C16	119.0 (9)
N2–C2–O2	117.5 (8)	C19–C18–C17	120.2 (9)
N2–C3–C4	110.0 (10)	C20–C19–C18	117.4 (9)
C5–C4–C3	104.1 (10)	N4–C20–C19	123.5 (8)
C6–C5–C4	111.6 (11)	C7–N1–C1	123.2 (9)
N2–C6–C5	105.6 (10)	C9–N1–C1	128.0 (9)
N1–C7–C8	108.8 (10)	C9–N1–C7	108.7 (9)
C10–C8–C7	107.4 (12)	C3–N2–C2	125.5 (8)
N1–C9–C10	106.8 (10)	C6–N2–C2	125.6 (9)
C9–C10–C8	108.3 (12)	C6–N2–C3	108.8 (8)
N3–C11–C15	121.7 (10)	C12–N3–C11	116.6 (9)
N3–C12–C13	123.4 (11)	C20–N4–C16	117.6 (8)
	Angles with Ni at Apex		
S2–Ni–S1	101.2 (2)	N4–Ni–S2	161.4 (3)
O1–Ni–S1	68.9 (2)	O2–Ni–O1	94.3 (2)
O2–Ni–S1	160.7 (3)	N3–Ni–O1	172.9 (3)
N3–Ni–S1	103.8 (3)	N4–Ni–O1	89.2 (2)
N4–Ni–S1	95.4 (2)	N3–Ni–O2	92.6 (2)
O1–Ni–S2	88.9 (2)	N4–Ni–O2	93.8 (3)
O2–Ni–S2	67.8 (2)	N4–Ni–N3	92.1 (2)
N3–Ni–S2	92.0 (2)		
	Other Angles in Chelate Ring		
N1–S1–C1	73.6 (4)	Ni–O1–C1	95.4 (5)
Ni–S2–C2	73.2 (5)	Ni–O2–C2	97.7 (5)

[a] Units: deg.

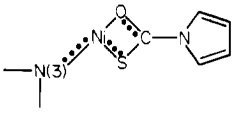
Table VI. Selected Bond Distances (Å) within Monothiocarbamates

compd	C–O	C–N	C–S	ref
$Ni(ptc)_2 \cdot 2py$[b]	1.231 (11)	1.392 (14)	1.713 (10)	*a*
$Ni(ptc)_2 \cdot 2py$[c]	1.254 (12)	1.409 (12)	1.675 (10)	*a*
$(Ni(n\text{-}Bu_2mtc)_2)_6$	1.227 (29)	1.364 (32)	1.775 (25)	5
$Co(pyrmtc)_2 \cdot 2pyr$	1.283 (7)	1.342 (7)	1.735 (6)	4
$Fe(Me_2mtc)_3$	1.278 (9)	1.329 (5)	1.733 (4)	3
$Zn(pipmtc)_2 \cdot 2pip$	1.24 (1)	1.36 (1)	1.75 (1)	8
$(Cu(n\text{-}Pr_2mtc))_6$	1.21 (3)	1.37 (4)	1.78 (3)	6
$Ti(Et_2mtc)_4$	1.275 (5)	1.337 (5)	1.721 (5)	9
$Zr(Et_2mtc)_4$	1.270 (4)	1.335 (4)	1.727 (4)	9
$Ti(Et_2mtc)_3Cl$	1.275 (5)	1.327 (5)	1.732 (5)	10
$UO_2(n\text{-}Pr_2mtc)_2(OC_2H_5)$	1.28 (2)	1.33 (2)	1.72 (2)	11

[a] This work. [b] Ligand 1. [c] Ligand 2.

Results and Discussion

The pyrrole-*N*-carbothioate ligand is bonded in a bidentate manner to the Ni(II), and with two pyridine molecules completing the coordination sphere, a distorted octahedral geometry exists. Tables IV and V list the intramolecular bond distances and angles, respectively, while the numbering scheme for the atoms is shown in Figure 1. The N4–Ni–S2 bond angle of 161.4 (3)° as well as the N3–Ni–S1 angle of 103.8 (3)° indicate the distortion from a pure octahedral geometry about the Ni atom. This distortion is primarily due to the small "bite" distance (S–O) of the monothiocarbamate ligand (2.587 for ligand 1, S1–O1; 2.557 for ligand 2, S2–O2). It is also interesting that no ligand donor atom is trans to a similar ligand donor atom. It is likely, since all steric effects seem to be equally unimportant in the various possible geometries, that the trans influence of the pyridines and perhaps the sulfur atoms control the coordination sphere arrangement. The classic polarization effect[23] of the trans influence favors a geometry with cis pyridines. Given a choice between oxygens and sulfurs trans to the pyridines, we would expect to find oxygens since they compete much less effectively for the π-electron density. This is not the case here and two explanations, while obviously related, are possible. First, such an arrangement would result in trans sulfur atoms which would not be favored by a trans-influence argument either. This explanation might be adequate for monodentate sulfur and oxygen donor ligands, but we have a much more interesting case here. Consider, for example, the long-range influence that py 1 (N3) has on S1 of ligand 1. If the Ni–N3 bond is stabilized by π bonding at the expense of the trans Ni–O1 bond, we might expect that to release π density to the C1–O1 bond in the chelate ring.



This apparently forces that ligand into a resonance structure which has features of that in IA and which allows the sulfur atom in this ligand to develop some multiple bond character with the Ni. This is seen in the shorter Ni–S1 bond distance of 2.426 (5) Å. The prospects for two such sulfurs to be trans to each other apparently is less favorable than having the remaining sulfur trans to a pyridine nitrogen. This latter

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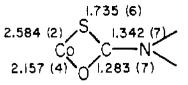
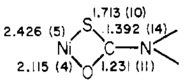
situation results in a longer Ni–S2 distance of 2.476 (5) Å.

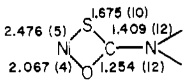
Our primary interest here is in the resonance structures within the ligand itself. As noted in the Introduction, a C–N single bond would rule out resonance form IC from the possible structures. Table VI lists C–N, C–S, and C–O bond distances for this structure and all other structures of monothiocarbamates reported to date. It is immediately clear that the average value for the two C–N bond distances in the two pyrrole-*N*-carbothioate ligands of 1.400 (8) Å is significantly larger than the values for any of the other 10 structures given. This value is much nearer to that of a standard C–N single-bond distance (1.47 Å) than to that of a C=N double-bond distance (1.27 Å).[24] This large average value for the C–N distance and the fact that the C–N distances in both ligands are statistically the same suggest that resonance form IC makes only a very modest contribution to the electronic structure of the coordinated ligand. Table VI also shows that the C–S distances in the pyrrole-*N*-carbothioate ligands are the shortest of any reported to date. In this case however, there is a large and statistically significant difference in the two values which is likely due to the trans influence of the nitrogens from pyridine.

Further evidence that a new predominant resonance form exists in this structure can be obtained by the comparison of corresponding bond distances in the cobalt pyrrolidine monothiocarbamate complex.[4]





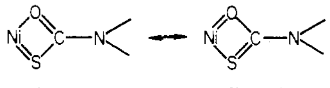
ligand 1



ligand 2

Even considering that Co(II) will have a larger covalent radius than Ni(II), *all* of the bond distances in the four-membered chelate ring are longer for the pyrrolidine structure than the pyrrole structure. This supports the concept of some degree of π delocalization in the Ni(II) structure.

Since it seems possible to consider the electronic structure of the Ni(COS) unit without including resonance contribution through the C–N bond, a comparison of the two four-membered Ni(COS) rings is interesting. We can actually consider the chelate ring to be somewhat between the two extreme resonance forms IA and IB.



ligand 1 ligand 2

This diagram does not represent true bond orders but rather trends in bond lengths ***between*** the two ligands here. In ligand 1, a shorter Ni–S bond is associated with a longer C–S bond, a shorter C–O bond, and a longer Ni–O bond.[25] Such a flexibility in electron density in this ring would only be associated with a large amount of delocalization in the COS unit.

Taken together, these data suggest that resonance form IB is the single largest contribution to the electronic structure of this new ligand, that form IC makes little contribution, and that, under the appropriate influence, form IA can also be important.

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Registry No. $Ni(ptc)_2(py)_2$, 81158-07-8; $Ni_2(ptc)_4{\cdot}THF$, 81177-87-9.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, anisotropic temperature factors (Table III), and hydrogen coordinates (Table VII) (14 pages). Ordering information is given on any current masthead page.

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(24) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 224–9.

(25) These differences are real statistically. The probability that the distances are the same are as follows: C–S <0.01; C–O <0.15; Ni–O <<0.0001; Ni–S <<0.0001. Normally, values of <0.05 are considered as criteria for real bond distance differences. The value for the C–O bond, while outside this limit, is valid when taken together with the three other bonds.[26]

(26) Stout, G. R.; Jensen, L. H. "X-Ray Structure Determination, A Practical Guide"; Macmillan: New York, 1969; pp 419–20.