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2-Pyrrolylthiones as Monoanionic Bidentate N,S-Chelators: Synthesis and Molecular Structure of 2-Pyrrolylthionato Complexes of Nickel(II), Cobalt(III), and Mercury(II)

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The metal-chelating ability of 2-pyrrolylthiones is described. The readily available ligands di-2-pyrrolyl thione (**6**), 2-thioacetylpyrrole (**10**), and 2-thiobenzoylpyrrole (**11**) constitute examples of monoanionic ligands with N,S-donor atom sets, although di-2-pyrrolyl thione (**6)** could theoretically also achieve chelation through an N,N-donor set. A square planar Ni(II) complex, **14**, an octahedral Co(III) complex, **18**, and a tetrahedral Hg(II) complex, **17**, with the di-2-pyrrolyl thionato chelate have been prepared, and their structures have been characterized by ^{1}H NMR, UV−vis, MS, IR, elemental analysis, and single-crystal X-ray diffraction. Crystal data for **14**: $C_{18}H_{14}N_4NiS_2 \cdot 0.28H_2O$, trigonal, $R\bar{3}$, $a = 18.467(1)$ Å, $b = 18.467(1)$ Å, $c = 26.404(2)$ Å, $V = 7797(1)$ Å^3; $Z = 18$, $R = 3.2\%$. Crystal data for **18-*mer***: $C_{27}H_{21}CoN_6S_3 \cdot C_3H_6O$ (acetone), monoclinic, $P21/n$, $a = 9.569(1)$ Å, $b = 23.152(1)$ Å, $c = 13.659(1)$ Å, $\beta = 100.882(8)°$, $V = 2971.6(5)$ Å^3, $Z = 4$, $R = 4.3\%$. Crystal data for **17**: $C_{18}H_{14}HgN_4S_2$, triclinic, $P\bar{1}$, $a = 8.443(2)$, $b = 14.278(1)$ Å, $c = 7.445(1)$ Å, $\alpha = 90.561(9)°$, $\beta = 97.64(1)°$, $\gamma = 104.250(9)°$, $V = 861.3(2)$ Å^3, $Z = 2$, $R = 4.2\%$. The bond lengths and angles of these metal complexes are comparable to those of known N,S-chelates. A comparison of the structural parameters of the ligand in the metal complexes with those for the free ligand **6** demonstrates the preorganization of the free ligand for complexation and demonstrates the spectator role of the noncoordinating pyrrolic unit. Chelation of Ni(II) by 2-thioacetylpyrrole (**10**) and 2-thiobenzoylpyrrole (**11**) to provide complexes **12** and **13** with structures analogous to complex **14** is also described.

Introduction

As recently pointed out by Vahrenkamp and co-workers, the chemistry of metal complexes with N,S-donor chelates is experiencing a renaissance.[1] This is in part due to their diverse roles in metalloenzymes and their varied catalytic and pharmacological properties. For instance, biomimetic models of metalloenzymes such as [NiFe] hydrogenase,[2] the blue copper proteins,[3] and aconitases[4] often employ, in resemblance to their natural counterparts, N,S-donor ligands. Cimetidine (**1**) (trade name Tagamet), used for the treatment of peptic ulcers, is proposed to exist as a copper(II) chelate under in vivo conditions.[5,6] Other drugs contain N,S-donor group ligands, such as the copper complex **2**.[7] The underlying chelate is being used to complex radioactive metal isotopes, for instance ^{99m}Tc or ^{62}Cu, and the complexes find uses as radioimaging agents.[8,9] Aryl carboxaldehyde thiosemicarbazones have shown activity against bacterial and viral infections, tuberculosis, rheumatism,

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[§] Deceased on Oct 27, 1998. This paper is dedicated to the memory of Steven J. Rettig.

(1) (a) Brand, U.; Burth, R.; Vahrenkamp, H. *Inorg. Chem.* **1996**, *35*, 1083. For representative examples of current research involving N,S-donor ligands see, e.g.: (b) Sellmann, D.; Sutter, J. In *Sulfur Coordinated Transition Metal Complexes: Biological and Industrial Significance*; Stiefel, E. J., Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; p 101. (c) Grapperhaus, C. A.; Darensbourg, M. Y. *Acc. Chem. Res.* **1998**, *31*, 451. (d) Hanss, J.; Krüger, H.-J. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 360. (e) Musie, G.; Reibenspies, J. H.; Darensbourg, M. Y. *Inorg. Chem.* **1998**, *37*, 302. (f) Sellmann, D.; Utz, J.; Heinemann, F. W. *Inorg. Chem.* **1999**, *38*, 459. (g) Bhattacharyya, S.; Weakley, T. J. R.; Chaudhury, M. *Inorg. Chem.* **1999**, *38*, 633. (h) Bohle, S. D.; Zafar, A.; Goodson, P. A.; Jaeger, D. A. *Inorg. Chem.* **2000**, *39*, 712.

(2) Halcrow, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1193.

(3) (a) Kitajima, N.; Fujisawa, K.; Tanaka, M.; Moro-oka, Y. *J. Am. Chem. Soc.* **1992**, *114*, 9232. (b) Olsson, M. H. M.; Ryde, U.; Roos, B. O.; Pierloot, K. J. *J. Biol. Inorg. Chem.* **1998**, *3*, 109. (c) Messerschmidt, A. *Struct. Bonding (Berlin)* **1998**, *90*, 37.

(4) Lauble, H.; Kennedy, M. C.; Beinert, H.; Stout, C. D. *Biochemistry* **1992**, *31*, 2735.

(5) Greenaway, F. T.; Brown, L. M.; Dabrowiak, J. C.; Thompson, M. R.; Day, V. M. *J. Am. Chem. Soc.* **1980**, *102*, 7782.

(6) Martinez, M. A.; Legros, J. P.; Soto, L.; Sancho, A. *Polyhedron* **1991**, *10*, 1031.

(7) John, E. K.; Green, M. A. *J. Med. Chem.* **1990**, *33*, 1704.

(8) O'Neil, J. P.; Wilson, S. R.; Katzenellenbogen, J. A. *Inorg. Chem.* **1994**, *33*, 319.

(9) Parker, D. *Chem. Br.* **1994**, *10*, 818.

(10) Knag, Y.; Yang, N.; Kang, S. O.; Ko, J.; Lee, C.-H.; Lee, Y.-H. *Organometallics* **1997**, *16*, 5522.

(11) Berkessel, A.; Hermann, G.; Rauch, O.-T.; Büchner, M.; Jacobi, A.; Huttner, G. *Chem. Ber.* **1996**, *129*, 1421.

(12) Akbar Ali, M.; Livingstone, S. E. *Coord. Chem. Rev.* **1974**, *13*, 101.

(13) Vagg, R. S. Bidentate Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 793−812.

(14) Livingstone, S. E. Other Sulfur-Containing Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 633−660.

(15) McAucliffe, C. A. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 165.

(16) Kuehn, C. A.; Isied, S. S. *Prog. Inorg. Chem.* **1980**, *27*, 153.

(17) Reedijk, S. E. Heterocyclic Nitrogen-Donor Ligands. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1987; Vol. 2, pp 73−98.

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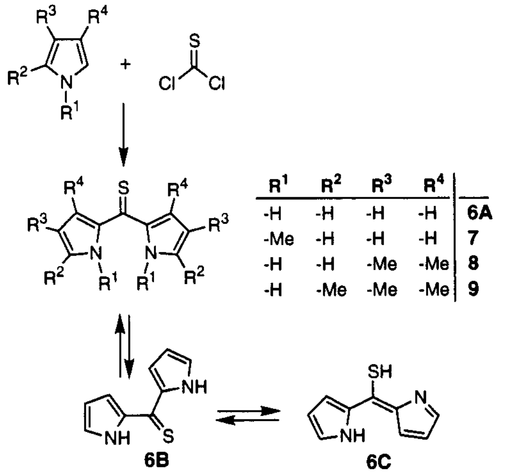
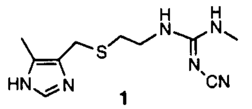
Scheme 1



R^1	R^2	R^3	R^4	
-H	-H	-H	-H	**6A**
-Me	-H	-H	-H	**7**
-H	-H	-Me	-Me	**8**
-H	-Me	-Me	-Me	**9**

and leprosy.[10] Interestingly, their Ni(II) complexes proved also to be active in the activation of Si−H bonds.[11]



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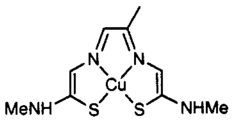

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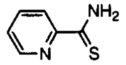

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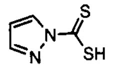

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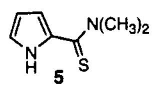

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A review pertaining to the topic of metal complexes of N,S-bidentate ligands was published by Akbar Ali and Livingston in 1974.[12] More recent reviews cover bidentate ligands in general[13] or certain sulfur-containing ligands.[14,15] An exhaustive review of the reactivity of the metal ion−sulfur bond was published by Kuehn and Isied in 1980,[16] including the transformation of a large number of S,N- and S,O-chelates. In the present context, a review by Reedijk,[17] covering heterocyclic nitrogen donor ligands, and one by Foulds,[18] summarizing the coordination chemistry of nickel, are of interest as well. A review of bioinorganic drugs, many of which contain N,S-donor ligands, was published most recently.[19]

Examples of N,S-bidentate ligands in which the nitrogen is part of a heterocycle and the sulfur donor atom is a thione or thiol include the compounds **3**,[12] **4**,[20] and thioamide **5**.[21] To the best of our knowledge, however, di-2-pyrrolyl thiones such as **6**−**9** (Scheme 1) have not been described in detail as metal-complexing agents before, although, in 1969, Clezy and Smythe noted in their paper describing the synthesis of di-2-pyrrolyl thiones that "like other members of the thione class [Andrieu, C., Mollier, Y., Lozac'h, N. *Bull. Soc. Chim. Fr.*, **1965**, 2457.] the dipyrrylthiones form complexes with mercuric chloride".[22] However, they did not provide an analysis or estimate of the nature of the complexes.

Our own interests in di-2-pyrrolylthiones lay in their use as starting materials for the synthesis of 5,15-diphenylporphyrin by means of the Raney nickel induced hydrodesulfurization of **6**, thereby obtaining di-2-pyrrolylmethane.[23] Reaction control of the hydrodesulfurization by TLC revealed at the onset of the reaction a dark green pigment. Its isolation and analysis led us to discover the complexing action of Ni(II) by di-2-pyrrolyl thiones.[24] This serendipitous finding then initiated a thorough investigation of the scope and limits of the use of 2-pyrrolylthiones as N,S-donor atom chelating agents for transition metals.

We now present the preparation and structural characterization of di-2-pyrrolyl thionato complexes of Ni(II), Co(III), and Hg(II). The metals were chosen as representative transition metals with preferred square planar, octahedral, and tetrahedral coordination environments. N-alkylation of the metal complexes demonstrates the spectator role of the noncoordinating pyrrolic unit in di-2-pyrrolyl thionato complexes. This, in turn, launched the investigation of 2-thioacetylpyrrole (**10**) and 2-thiobenzoylpyrrole (**11**) as N,S-bidentate ligands for Ni(II), the results of which will also be presented.

Experimental Section

Instrumentation and Methodologies. Melting points were determined on a Thomas model 40 micro hot stage, and are uncorrected. IR spectra were measured with a Perkin-Elmer model 834 FT-IR instrument. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AC-200 or AMX 500 or a Varian XL-300. The NMR spectra are expressed on the δ scale and were referenced to residual solvent peaks. UV−vis spectra were measured on a Hewlett-Packard HP 8452A photodiode array spectrophotometer in the solvents indicated. Low- and high-resolution mass spectra were obtained by the University of British Columbia (UBC) departmental mass spectrometry facilities, and elemental analyses were performed by the microanalytical laboratory at UBC.

Materials. The silica gel used for flash chromatography was Merck silica gel 60, 230−400 mesh. R_f values were measured on Merck silica TLC aluminum sheets (silica gel 60 F_{254}), while preparative TLC was performed on precoated 20 × 20 cm (1000 μm thickness) Merck silica gel glass plates. Dipyrrolylthiones **6**−**9** were prepared according to Clezy and Smythe.[22] 2-Thioacetylpyrrole[25] (**10**) and 2-thiobenzoylpyrrole[26] (**11**) were prepared by oxygen-to-sulfur exchange from the corresponding known ketones.[27−29] Synthetic procedures and full analytical and spectroscopic data for **10** and **11** are provided in the Supporting Information. All reagents and solvents were commercially available, were of reagent grade or higher, and were used as received.

(SP-4-*trans*)-Bis(2-pyrrolyl-2′-pyrrolylato-*κN*-thione-*κS*)nickel(II) (14). General Procedure. Thione **6** (0.5 g, 2.84 mmol) dissolved in MeOH (10 mL) was mixed with a solution of nickel(II) acetate·$4H_2O$ (2.5 g, 6.02 mmol) in MeOH (20 mL) and concentrated NH_4OH (0.2 mL). Rapid precipitation of a dark solid occurred. The mixture was stirred for 12 h and the solid filtered off, dried, and purified by means of either column chromatography (silica gel−$CHCl_3$) or repeated (3−4 times) recrystallization by slow solvent exchange on a rotary evaporator from CH_2Cl_2 to hexane. Depending on the method chosen, up to 450 mg (78%) of an analytically pure dark green crystalline material with a metallic shine was obtained: mp 273 °C dec; R_f = 0.45 (1:1 CCl_4/CH_2Cl_2); ^{1}H NMR (500 MHz, acetone-d_6) δ 6.36 (dd, J = 1.6, 5.8 Hz, 1H), 6.44 (m, 1H), 7.22 (dd, J = 0.9, 4.5 Hz, 1H), 7.24 (m, 1H), 7.32 (tr, J = 1.4 Hz, 1H), 7.37 (m, 1H), 11.2 (br s, 1H, exchangeable with D_2O); ^{13}C NMR (75 MHz, acetone-d_6) δ 113.4,

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(18) Foulds, G. A. *Coord. Chem. Rev.* **1990**, *98*, 1.

(19) *Chem. Rev.* **1999**, *99*, 9 (Medicinal Inorganic Chemistry thematic issue).

(20) Trofimenko, S. *Chem. Rev.* **1972**, *72*, 497.

(21) Fukazawa, M.; Kita, M.; Nonoyama, M. *Polyhedron* **1994**, *13*, 1609.

(22) Clezy, P. S.; Smythe, G. A. *Aust. J. Chem.* **1969**, *22*, 239.

(23) Brückner, C.; Posakony, J. J.; Johnson, C. K.; Boyle, R. W.; James, B. R.; Dolphin, D. *J. Porphyrins Phthalocyanines* **1998**, *2*, 455.

(24) (a) Brückner, C.; Dolphin, D. *Abstracts of Papers*, Pacifichem '95, Honululu, HI, Dec 17−22, 1995; INORG 445. (b) Brückner, C. Ph.D. Thesis, University of British Columbia, Vancouver, 1996.

(25) Murase, M.; Yoshida, S.; Hosaka, T.; Tobinaga, S. *Chem. Pharm. Bull.* **1991**, *39*, 489.

(26) Lumbroso, H.; Liégeois, C.; Pappalardo, G. C.; Andrieu, C. G. *J. Mol. Struct.* **1984**, *112*, 85.

(27) Schweizer, E. E.; Light, K. K. *J. Org. Chem.* **1966**, *31*, 2912.

(28) Cadamuro, S.; Degani, I.; Dughera, S.; Fochi, R.; Gatti, A.; Piscopo, L. *J. Chem. Soc., Perkin Trans. 1* **1993**, 273.

(29) Barbero, M.; Cadamuro, S.; Degani, I.; Fochi, R.; Gatti, A.; Regondi, V. *J. Org. Chem.* **1988**, *53*, 2245.

113.5, 117.6, 119.4, 123.3, 128.7, 128.8, 148.9, 151.0, 175.9; UV−vis (acetone) λ_{max} (log ϵ) 366 (4.38), 434 (4.75), 530 (4.23) nm; MS (EI, 220 °C) *m*/*e* 408 (100, M^+), 374 (17.2), 341 (8.5), 288 (76.3), 176 (55.4, ligand$^+$); IR (KBr) 3394 (s), 3343 (s), 1522 (s), 1394 (s), 1381 (s), 1279 (s), 1103 (s), 1066 (m), 1023 (s), 980 (m), 901 (m), 884 (m), 833 (w), 799 (w), 740 (s), 710 (s), 645 (s) cm^{-1}. Anal. for $C_{18}H_{14}N_4NiS_2$, calcd (found): C, 52.84 (53.10); H, 3.45 (3.46); N, 13.69 (13.35); S, 15.67 (14.83).

(SP-4-*trans*)-[(2-Pyrrolyl-2′-pyrrolylato-κ*N*-thione-κ*S*){2-(1-methyl)pyrrolyl-2′-pyrrolylato-κ*N*-thione-κ*S*}]nickel(II) (15) and (SP-4-*trans*)-Bis[2-(1-methyl)pyrrolyl-2′-pyrrolylato-κ*N*-thione-κ*S*]nickel(II) (16). Complex **14** (200 mg, 3.94 × 10^{-4} mol) was suspended under anhydrous conditions in dry THF (25 mL). A 1.6 M solution of *n*-BuLi in THF (3.0 mL, 1.2 equiv) was added by syringe into the cooled (−78 °C) solution, upon which all remaining solids dissolved. After the solution was stirred for 1 h, MeI (30 μL, 1.2 equiv) was injected, and the resulting solution was allowed to warm to rt. MeOH (1 mL) was added, followed by $CHCl_3$ (50 mL). The mixture was washed with water and the organic phase dried over Na_2SO_4 and subjected to preparative TLC (silica gel, CH_2Cl_2/CCl_4, 1:3). Three brown bands became visible. They were isolated, eluted with CH_2Cl_2, and evaporated to dryness. The least polar compound was starting material (30 mg, 15% recovery), the second band was the mono-N-methylated product **15** (125 mg, 61% yield), and the third, most polar compound was identified as the bis-N-methylated product **16** (20 mg, 9%). The outcome was changed to **14** (5% recovery), **15** (22%), and **16** (55%) if, under otherwise identical conditions, 2.4 equiv of *n*-BuLi and MeI were used. Data for **15**: mp 200 °C dec; $R_f = 0.85$ (1:1 CCl_4/CH_2Cl_2); brown color; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.07 (s, 3H), 6.23 (s, 1H), 6.25−6.4 (m, 2H), 6.45 (s, 1H), 6.68 (s, 1H), 6.85−7.0 (m, 3H), 7.11 (s, 1H), 7.20 (s, 1H), 7.40−7.45 (m, 2H), 9.6 (br s, 1H); UV−vis ($CHCl_3$) λ_{max} (rel intens) 368 (0.47), 434 (1.0), 534 (0.33) nm; LR-MS (EI, 200 °C) *m*/*e* 422 (100, M^+), 408 (36, $M^+ - CH_2$), 246 (28), 189 (88, methylated ligand), 176 (63, non-methylated ligand); HR-MS (EI, 200 °C) *m*/*e* calcd for $C_{18}H_{14}N_4NiS_2$ 422.0170, found 422.0157. Data for **16**: mp = 220 dec; $R_f = 0.65$ (1:1 CH_2Cl_2/CCl_4); ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.01 (s, 3H), 6.23 (s, 1H), 6.32 (s, 1H), 6.68 (s, 1H), 6.85 (s, 1H), 7.00 (s, 1H), 7.47 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 33.2, 105.1, 114.1, 120.8, 127.8, 131.2, 146.2, 149.9, 151.1, 178.0; UV−vis (CH_2Cl_2) λ_{max} (rel intens) 368 (0.53), 432 (1.0), 543 (0.39) nm; LR-MS (EI, 150 °C) *m*/*e* 436 (100, M^+), 421 (9.2, $M^+ - CH_3$), 403 (6.2), 248 (25.6, M^+ − ligand), 189 (ligand$^+$); HR-MS (EI, 150 °C) *m*/*e* calcd for $C_{20}H_{18}N_4NiS_2$ 436.0326, found 436.0328.

(SP-4-*trans*)-Bis[2-(3,4-dimethyl)pyrrolyl-2′-(3,4-dimethyl)pyrrolylato-κ*N*-thione-κ*S*]nickel(II). This complex was prepared from thione **8** and nickel(II) acetate in 30% yield as described for the formation of **14**: $R_f = 0.33$ (1:1 CCl_4/CH_2Cl_2); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.80 (s, 3H), 1.85 (s, 3H), 2.02 (s, 3H), 2.10 (s, 3H), 6.76 (s, 1H), 6.78 (s 1H), 7.30 (s, 1H), 8.12 (s, 1H), 9.3 br s (1H); UV−vis ($CHCl_3$) λ_{max} (rel intens) 360 (sh), 424 (1.0), 508 (0.52); LR-MS (EI, 200 °C) *m*/*e* 520 (12.6, M^+), 505 (0.9, $M^+ - CH_3$), 459 (9.1), 424 (7.8, M^+ − dimethylpyrrole), 410 (4.4), 337 (9.1, M^+ − ligand), 322 (7.6, M^+ − ligand − CH_3), 232 (45.1), 184 (100, ligand$^+$); HR-MS (EI, 200 °C) *m*/*e* calcd for $C_{26}H_{30}N_4{}^{58}NiS_2$ 520.1265, found 520.1259.

(SP-4)-Bis[2-pyrrolylato-κ*N*-thioacetyl-κ*S*]nickel(II) (12). 12 was prepared in 81% yield from thione **10** and nickel(II) acetate according to the general procedure. Slow evaporation of a MeOH solution yielded fine long dark red needles: mp 212−214 °C (phase transition—as seen through the microscope—at 177 °C); $R_f = 0.90$ ($CHCl_3$); deep red color; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.84 (s, 3H), 6.25 (d, $J = 4.4$ Hz, 1H), 6.81 (m, 1H), 7.42 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.7, 119.3, 123.5, 152.3, 155.6, 191.7; UV−vis (log ϵ) λ_{max} 282 (4.48), 370 (4.32), 474 (3.99), 496 (sh), 578 (3.58) nm; LR-MS (EI, 150 °C) *m*/*e* 306 (100, M^+), 291 (15.6, $M^+ - CH_3$), 246 (18.3), 182 (27.8), 92 (67.0); HR-MS (EI, 150 °C) *m*/*e* calcd for $C_{12}H_{12}N_2{}^{58}NiS_2$ 305.9795, found 305.9803; IR (KBr) 1569 (s), 1383 (s), 1308 (w), 1150 (w), 1110 (m) 886 (w), 824 (m), 741 (m), 674 (w) cm^{-1}. Anal. for $C_{12}H_{12}N_2NiS_2$, calcd (found): C, 46.94 (47.13); H, 3.94 (3.69); N, 9.12 (8.92).

(SP-4)-Bis(2-pyrrolylato-κ*N*-thiobenzoyl-κ*S*)nickel(II) (13). 13 was prepared in 80% yield from thione **11** (100 mg) and nickel(II) acetate in the presence of oxygen according to the general procedure. Chromatography on a short column of silica gel with CH_2Cl_2 as eluent was used to purify the complex. The first, purple fraction was collected and evaporated in vacuo to yield **13** as analytically pure microscopically fine dark purple needles: $R_f = 0.92$ (CH_2Cl_2/CCl_4 1:1); dark purple color; mp 234 °C dec; ^{1}H NMR (200 MHz, dioxane-d_8) δ 6.45 (dd, $J = 4.0$, 1.5 Hz, 2H), 6.90 (dd, $J = 4.0$, 1.5 Hz, 2H), 7.45−7.60 (m, 6H), 7.68 (s, 2H), 7.85 (dd, $J = 8.0$, 2 Hz, 4H); UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 312 (4.68), 390 (4.38), 506 (sh), 526 (4.00), 604 (sh) nm; LR-MS (EI, 150 °C) 430 (100, M^+), 397 (19.5), 308 (17.0), 245 (19.1, MH^+ − ligand), 186 (33.6, ligand), 154 (64.3); HR-MS (EI, 150 °C) *m*/*e* calcd for $C_{22}H_{16}N_2{}^{59}NiS_2$ 430.0108, found 430.0104; IR (KBr) 1548 (s), 1382 (s), 1294 (w), 1062 (m), 969 (m) 762 (m), 758 (w), 688 (m), 684 (m) cm^{-1}. Anal. for $C_{22}H_{16}N_2NiS_2$, calcd (found): C, 61.28 (61.17); H, 3.74 (3.53); N, 6.50 (6.42).

(T-4)-Bis(2-pyrrolyl-2′-pyrrolylato-κ*N*-thione-κ*S*)mercury(II) (17). 17 was prepared from mercury(II) acetate and thione **6** according to the general procedure. The precipitated crude metal complex was filtered, dried, loaded onto a short column of silica gel, and eluted with CH_2Cl_2. Slow evaporation of the fluorescent yellow CH_2Cl_2 solution yielded **17** as analytically pure shiny yellow hexagonal plates (33% yield). The product is well soluble only in polar solvents such as acetic acid, pyridine, or DMSO. Data for **17**: mp = 181 °C dec; $R_f = 0.45$ (CH_2Cl_2); brilliant yellow color; ^{1}H NMR (300 MHz, DMSO-d_6) δ 4.39 (s, 2H), 6.71 (d, $J = 2.7$ Hz, 2H), 6.98 (s, 2H), 7.30 (s, 2H), 7.38 (d, $J = 3.3$ Hz, 2H), 7.58 (s, 2H), 11.95 (s, 2H); ^{13}C NMR (75 MHz, pyridine-d_5) δ 112.3, 118.4, 121.8, 127.0, 127.0, 127.7, 146.9, 151.2, 173.4; UV−vis (CH_2Cl_2) λ_{max} (log ϵ) 402 (4.77), 452 (4.78) nm; IR (KBr) 3401 (s), 3334 (s), 1539 (m), 1513 (s), 1481 (m), 1405 (w), 1370 (s), 1347 (s), 1290 (w), 1255 (m), 1195 (w), 1124 (s), 1031 (s), 988 (m), 895 (s), 879 (m), 866 (m), 810 (s), 767 (m), 742 (s), 694 (m) cm^{-1}. Anal. for $C_{18}H_{14}N_4HgS_2$, calcd (found): C, 39.23 (38.88); H, 2.56 (2.61); N, 10.17 (9.85).

(OC-6-*mer*)-Tris(2-pyrrolyl-2′-pyrrolylato-κ*N*-thione-κ*S*)cobalt(III) (18-*mer*) and (OC-6-*fac*)-Tris(2-pyrrolyl-2′-pyrrolylato-κ*N*-thione-κ*S*)cobalt(III) (18-*fac*). Reaction of thione **6** with cobalt(II) acetate in the presence of oxygen according to the general procedure produced a solid material which was prepurified by column chromatography (silica−$CHCl_3$) and then subjected to preparative TLC (CH_2Cl_2/CCl_4, 1:3, multiple developments). The least polar, brown-orange band gave 22% **18-*mer*** and the second, orange band 19% **18-*fac***. Data for **18-*mer***: slow evaporation of an acetone solution yielded dark ruby red X-ray-quality crystals; mp 150 °C dec; $R_f = 0.25$ (CH_2Cl_2/CCl_4); ^{1}H NMR (300 MHz, acetone-d_6) δ 5.95 (s, 1H), 6.35−6.42 (m, 6H), 6.56 (dd, $J = 1.2$, 4.2 Hz, 1H), 7.10−7.20 (m, 3H), 7.24−7.30 (m, 2H), 7.34−7.37 (m, 2H), 7.46 (dd, $J = 1.2$, 4.5 Hz, 1H), 7.67 (s, 1H), 7.91 (s, 1H), 11.0 (br s, 3H); ^{13}C NMR (50 MHz, acetone-d_6) δ 112.1, 112.2, 112.3, 114.8, 114.9, 115.4, 120.4 (multiplet), 120.7, 123.3, 124.1 (multiplet), 126.9, 127.0 (multiplet), 131.6 (multiplet), 145.8, 147.7, 147.9, 151.1, 151.2, 151.4, 178.2, 178.4, 178.7; UV−vis ($CHCl_3$) λ_{max} 416 nm; LR-MS (FAB, 3-NBA matrix) 643 (3.5, M^+ + Co), 585 (5.3, MH^+), 409 (100, M^+ − ligand), 343 (23.0), 234 (78.1); LR-MS (FAB, 3-NBA matrix) *m*/*e* calcd for $C_{27}H_{21}N_6{}^{59}CoS_3$ 584.03218, found 584.03505; IR (KBr) 3397 (s), 3345 (s), 1544 (m), 1517 (s), 1420 (s), 1372 (s), 1345 (s), 1308 (m), 1267 (m), 1117 (m), 1105 (m), 1172 (w), 1160 (w), 1031 (m), 997 (m), 908 (m), 878 (m), 815 (m), 747 (m), 698 (w) cm^{-1}. Anal. for $C_{27}H_{21}N_6CoS_3\cdot{}^1/_2H_2O$, calcd (found): C, 54.63 (54.34); H, 3.74 (3.66); N, 14.16 (13.84). Data for **18-*fac***: mp 170 °C dec; $R_f = 0.12$ (CH_2Cl_2/CCl_4); dark orange color; ^{1}H NMR (200 MHz, acetone-d_6) δ 5.37 (s, 3H), 5.57 (m, 3H), 5.72 (dd, $J = 1.5$, 4.2 Hz, 3H), 6.35 (m, 3H), 6.44 (s, 3H), 6.66 (d, 4.2H, 3H), 11.0 (br s, 3H); UV−vis ($CHCl_3$) λ_{max} 424 nm; LR-MS (FAB, 3-NBA matrix) *m*/*e* 643 (4.1, M^+ + Co), 584 (3.5, MH^+), 584 (3.3, M^+), 409 (100, M^+ − ligand), 343 (23.2), 234 (76.1); HR-MS (FAB, 3-NBA matrix) *m*/*e* calcd for $C_{27}H_{21}N_6{}^{59}CoS_3$: 584.03280, found 584.03184; IR (KBr) 3396 (s), 3343 (s), 1551 (s), 1527 (m), 1429 (s), 1378 (m), 1347 (s), 1304 (m), 1269 (m), 1204 (w), 1121 (m), 1104 (m), 1192 (m), 1165 (m), 1042 (s), 1006 (m), 910 (m), 876 (w), 813 (m), 740 (s), 688 (m) cm^{-1}. Anal. for $C_{27}H_{21}N_6CoS_3$, calcd (found): C, 55.47 (55.04); H, 3.62 (3.72); N, 14.38 (14.11).

X-ray Crystallography. Crystallographic data and selected experimental details are listed in Table 1. Selected bond lengths for the

Table 1. Summary of Crystallographic Data[a]

	14·0.28H$_2$O	**18**-*mer*·Me$_2$CO	**17**
empirical formula	C$_{18}$H$_{14}$N$_4$NiS$_2$·0.28H$_2$O	C$_{27}$H$_{21}$CoN$_6$S$_3$·C$_3$H$_6$O	C$_{18}$H$_{14}$HgN$_4$S$_2$
mol wt	414.25	642.70	551.05
cryst syst	trigonal	monoclinic	triclinic
space group	$R\bar{3}$ (no. 148)	$P21/n$ (no. 14)	$P\bar{1}$ (no. 2)
a, Å	18.467(1)	9.569(1)	8.443(2)
b, Å	18.467(1)	23.152(1)	14.278(1)
c, Å	26.404(2)	13.659(1)	7.445(1)
α, deg	90	90	90.561(9)
β, deg	90	100.882(8)	97.64(1)
γ, deg	120	90	104.250(9)
V, Å^3	7797(1)	2971.6(5)	861.3(2)
Z	18	4	2
ρ_{calcd}, g/cm^3	1.588	1.436	2.125
radiation (λ, Å)	Cu (1.541 78)	Mo (0.710 69)	Mo (0.710 69)
μ, cm^{-1}	39.47	8.11	92.10
transm factors	0.77−1.00	0.93−1.00	0.40−1.00
R^b (R_w)^c	0.032 (0.033)	0.043 (0.038)	0.042 (0.040)

[a] Obtained at $T = 294$ K. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths in **14** with Estimated Standard Deviations in Parentheses

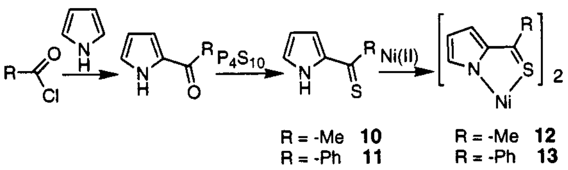
bond	distance (Å)	bond	distance (Å)
Ni(1)−S(1)	2.1988(9)	C(1)−C(9)	1.380(4)
Ni(1)−S(2)	2.1740(9)	C(2)−C(3)	1.355(4)
Ni(1)−N(1)	1.871(2)	C(3)−C(4)	1.416(4)
Ni(1)−N(3)	1.869(2)	C(5)−C(6)	1.377(4)
S(1)−C(9)	1.724(3)	C(5)−C(9)	1.432(4)
S(2)−C(18)	1.711(3)	C(6)−C(7)	1.391(4)
N(1)−C(1)	1.394(3)	C(7)−C(8)	1.356(5)
N(1)−C(4)	1.332(3)	C(10)−C(11)	1.408(4)
N(2)−C(5)	1.379(4)	C(10)−C(18)	1.408(4)
N(2)−C(8)	1.357(4)	C(11)−C(12)	1.360(5)
N(3)−C(10)	1.387(4)	C(12)−C(13)	1.392(4)
N(3)−C(13)	1.332(4)	C(14)−C(15)	1.389(4)
N(4)−C(14)	1.372(4)	C(14)−C(18)	1.415(4)
N(4)−C(17)	1.349(4)	C(15)−C(16)	1.376(5)
C(1)−C(2)	1.420(4)	C(16)−C(17)	1.356(5)

Table 3. Selected Bond Lengths in **17** and **18-*mer*** with Estimated Standard Deviations in Parentheses

17		**18-*mer***	
bond	distance (Å)	bond	distance (Å)
Hg(1)−S(1)	2.457(2)	Co(1)−S(1)	2.247(1)
Hg(1)−S(2)	2.450(2)	Co(1)−S(2)	2.254(1)
Hg(1)−N(1)	2.314(6)	Co(1)−S(3)	2.232(1)
Hg(1)−N(3)	2.330(6)	Co(1)−N(1)	1.927(3)
S(1)−C(9)	1.736(7)	Co(1)−N(3)	1.944(3)
S(2)−C(18)	1.730(7)	Co(1)−N(5)	1.908(4)
		S(1)−C(9)	1.690(4)
		S(2)−C(18)	1.722(4)
		S(2)−C(27)	1.709(4)

compounds appear in Tables 2 and 3. The final unit cell parameters were obtained by least squares on the setting angles for 25 reflections with $2\theta = 57.6-75.6°$ for 14, 26.1−38.2° for **17**, and 23.0−31.3° for **18-*mer***. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, remained constant for the three compounds. The data were processed and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans). The structure of **14** was solved by direct methods, and those of **17** and **18-*mer*** were solved by conventional heavy atom methods, the heavy atom coordinates being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Structure analyses of **14** and **17** were initiated in the centrosymmetric space groups $R\bar{3}$ and $P\bar{1}$, respectively, on the basis of the E statistics and the appearances of the Patterson functions. These choices were confirmed by the subsequent successful solutions and refinements of the structures.[30] Crystals of **14** contain 0.28 water molecule/nickel complex, located on the 3-fold axis. The population parameter for the oxygen atom was refined. Complex **18-*mer*** crystallizes as an acetone solvate.

Scheme 2



All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms in the complexes were fixed in calculated positions (N−H = 0.91 Å, C−H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). The hydrogen atoms associated with the water molecule in **14** were not included in the model. Secondary extinction corrections (Zachariasen type 2 isotropic) were applied where appropriate, the final values of the extinction coefficient being $2.6(3) \times 10^{-6}$ for **17**. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the *International Tables for X-ray Crystallography*.[31,32]

Results and Discussion

Syntheses of the Di-2-pyrrolyl Thiones. The syntheses of the crystalline, deep orange to red di-2-pyrrolylthiones **6**−**9** from thiophosgene and the corresponding pyrroles were performed according to procedures described in the literature (Scheme 1).[22,33] The reaction of the parent unsubstituted pyrrole was, on the basis of the original procedure, scaled up 10-fold, yielding ∼20 g of crystalline material without any problems in reaction control or loss of yield. The preparation of 2-thioacetylpyrrole (**10**)[25] as a red oil and the red solid 2-thiobenzoylpyrrole (**11**)[26] was accomplished by an oxygen-to-sulfur exchange of the corresponding ketones with P$_4$S$_{10}$ or Lawesson's reagent (2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-phosphetane-2,4-disulfide)[34] according to procedures similar to the ones provided in the literature (Scheme 2). Since the characterization of these thiones is incomplete in the original literature, we describe improved synthetic procedures and full analytical and spectroscopic data for **10** and **11** in the Supporting Information.

Solution- and Solid-State Structure of Di-2-pyrrolyl Thione (6). Di-2-pyrrolyl thione (**6**) could theoretically exist in various conformations, each in several tautomeric forms (**6A**−**6C**). Dipole moment studies of di-2-pyrrolyl ketone and the corresponding thione **6** have shown, however, that the preferred solution-state conformation in several nonpolar solvents is the uniplanar conformation **6B** in which the carbonyl or thiocarbonyl group is on the same side of the molecule as the nitrogens.[26] On the basis of IR and UV−vis evidence, Clezy determined the dominant tautomer to be that of the thione **6A/B** rather than that corresponding to the *meso*-thioldipyrrin **6C**.[22] This preference is also found in the solid-state structure of both the thioketone **6** and the corresponding di-2-pyrrolyl ketone.[35]

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(30) teXan: Crytal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1985, 1992.

(31) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV.

(32) *International Tables for Crystallography*; Kluwer Academic Publishers: Boston, 1992; Vol. C.

(33) de Groot, J. A.; van der Steen, R.; Fokkens, R.; Lugtenburg, J. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 35.

(34) Cava, M. C.; Levinson, M. I. *Tetrahedron* **1985**, *22*, 5061.

(35) (a) Norsten, T. B.; McDonald, R.; Branda, N. R. *Chem. Commun.* **1999**, 719. (b) Cf. to the structure of α-substituted di-2-pyrrolylketones: Sheldrick, W. S.; Becker, W.; Engel, J. *Acta Crystallogr., Sect. B* **1978**, *34*, 2929.

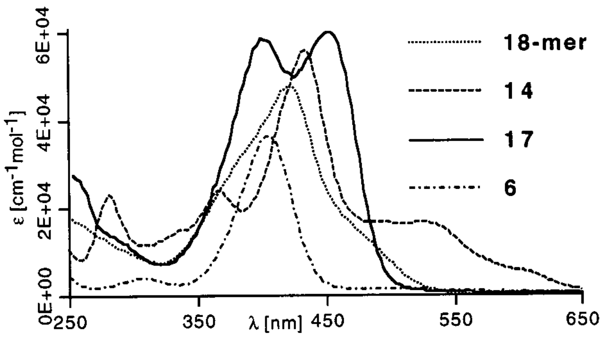
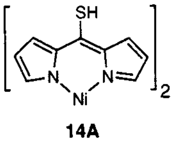


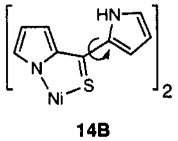
Figure 1. Optical spectra (CH_2Cl_2) of Ni(II) complex **14**, Hg(II) complex **17**, and Co(III) complexe **18-*mer*** in comparison to that of the free ligand **6**.

Reaction of Di-2-pyrrolyl Thione 6 with Ni(II). A mixture of a methanol solution of thione **6** with a methanolic nickel(II) acetate solution results, after the addition of a base such as NH_4OH, in the quantitative conversion and precipitation of the thione as nickel complex **14**. Recrystallization produces beautiful dark green crystals with a metallic sheen which are air and water stable. The mass spectrum and elemental analysis of the pigment showed the composition $C_{18}H_{14}N_4NiS_2$, corroborating the formulation of **14** as a neutral Ni(II) complex with two pyrrolythionato ligands. The bis-N-methylated thione **7** is inert toward Ni(II) under identical conditions, indicating the involvement of at least one pyrrole nitrogen in the coordination action of **6** with the metal ion. This reaction is unique to pyrrolylthione **6** in that the corresponding pyrrolylketone failed, under identical conditions, to produce any complex.

The electronic spectrum of the orange solution of complex **14** is shown in Figure 1. The spectrum is dominated by bands attributable to intraligand $p \rightarrow p^*$ transitions and possibly ligand-to-metal CT bands. Sharp NMR signals for this Ni(II) complex could be obtained, indicating the diamagnetic low-spin configuration of the Ni(II) ion, characteristic of a (pseudo) square planar coordination environment of the metal.[36] The formation of a diamagnetic complex with Ni(II) is, given the known examples of octahedral paramagnetic complexes with N,S-donor atom chelates, not necessarily expected.[6,37] Two modes of chelation could be attained by thiones of type **14**, namely, **14A**, in which the ligand chelates in an N,N-donor fashion like a dipyrrinato moiety,[38−40] or **14B**, in which the thione tautomer coordinates as an N,S-bidentate chelate. The IR indicates the presence of a pyrrolic NH functionality (IR (KBr) 3394 (s), 3343 (s) cm^{-1}),[41] supporting an N,S-coordination mode. Two independent and nonequivalent pyrrolic units can be clearly distinguished in the NMR spectra (^1H, ^{13}C, and particularly C,H- and H,H-COSY) of the complex. High- and low-temperature NMR studies did not indicate the presence of any dynamic effects such as intraligand donor exchanges. Thus, isomer **14B** is believed to represent the solution structure of **14**. This assignment allows the ligands to adopt a conformation very similar to the solution- and solid-state conformation of the free ligand. In principle, *cis*- and *trans*-isomers of the square planar Ni(II) complexe **14B** are possible, but electronic factors and interligand steric interactions make the *trans*-isomer the most likely. Indeed, an X-ray crystal structure analysis of **14** confirms this.



14A



14B

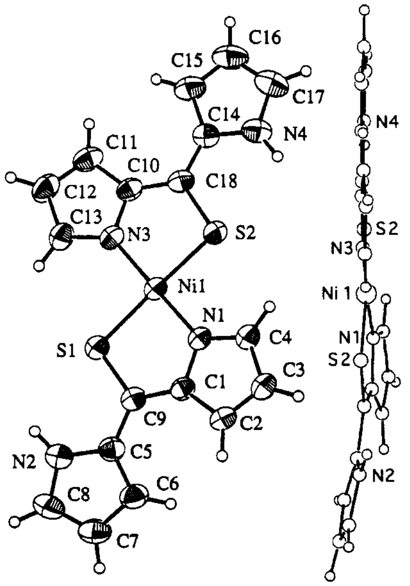


Figure 2. ORTEP representation (33% probability level) and numbering scheme, top and side views, for bis(di-2-pyrrolylthionato)nickel(II) complex **14**.

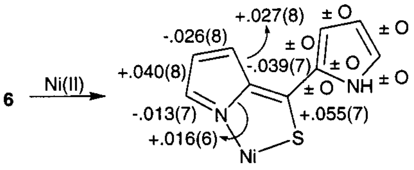


Figure 3. Bond lengths and angle changes of di-2-pyrrolyl thione (**6**) upon chelation to Ni(II). The changes were determined by comparison of the corresponding average bond lengths in the solid-state structure of **6**[35a] and **14**.

A crystal suitable for X-ray crystallography was grown by slow evaporation of an acetone solution of the nickel complex **14**. Crystallographic data and selected bond distances are listed in Tables 1 and 2. The ORTEP representation and a side view of the complex are shown in Figure 2. As anticipated, the nickel center in pigment **14** is coordinated in an almost perfect square planar fashion by an N,S-donor set, arranged in the *trans*-configuration. Upon metalation, the ligands underwent some bond length changes which can be rationalized by the increased weight of the limiting resonance structure indicated (Figure 3). The bond lengths in the noncoordinating pyrrolic unit remain unchanged upon metal complex formation; it thus appears nonparticipating in the operation of complexation. The interplanar angles between the two pyrrolic units in each chelating unit in the complex are markedly flattened (23° and 5.3°, respectively) when compared to that of the free ligand (31.9°).[35]

N-methylation of Complex 14. The spectator role of the noncomplexing pyrrolic unit raises the question of whether it is possible to chemically modify this unit without disturbing

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(36) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1999.

(37) Smits, J. M. M.; Janssen, R.; Beurskens, P. T.; van Ryin, J.; Reedijk, J. *Polyhedron* **1987**, *6*, 1843.

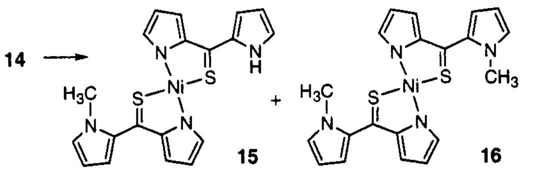
(38) (a) Brückner, C.; Karunaratne, V.; Rettig, S. J.; Dolphin, D. *Can. J. Chem.* **1996**, *74*, 2182. (b) Brückner, C.; Zhang, Y.; Rettig, S. J.; Dolphin, D. *Inorg. Chim. Acta* **1997**, *236*, 279.

(39) Zhang, Y.; Thompson, A.; Rettig, S. J.; Dolphin, D. *J. Am. Chem. Soc.* **1998**, *120*, 13537.

(40) Falk, H. *The Chemistry of Linear Oligopyrroles and Bile Pigments*; Springer-Verlag: Wien, New York, 1989.

(41) Hediger, H. J. *Infrarotspektroskopie*; Akademische Verlagsgesellschaft: Frankfurt a.M., 1971.

Scheme 3



the complexation. Another question is whether this unit could be omitted altogether (vide infra). Both questions can be answered affirmatively. Deprotonation of complex **14** with BuLi and subsequent reaction with 1 or 2 equiv of MeI results cleanly in the formation of the mono- and di-N-methylated products **15** and **16**, respectively (Scheme 3). The mass spectra of **15** and **16** show the expected mass gain of 14 and 28 mu, and the compounds could also be unambiguously identified by their ^{1}H NMR spectra. The C_2 symmetry of **16** is reflected in a simple, starting-material-like spectrum with an additional signal for the methyl groups, and the spectrum of compound **15** carrying two nonequivalent ligands is correspondingly more complex.

Reaction of 2-Thiacetylpyrrole (10) and 2-Thiobenzoylpyrrole (11) with Ni(II). The recognition of the innocent role of the noncomplexing pyrrolic unit in all of the dipyrrolylthionato complexes described raised the question of whether molecules containing solely the 2-pyrrolylthione moiety would be capable of forming complexes. Potential ligands of this class are, for instance, the known compounds 2-thioacetylpyrrole (**10**)[25] and 2-thiobenzoylpyrrole (**11**).[26] Indeed, the Ni(II) complexes **12** and **13** form in high yield upon mixing of basic methanolic solutions of the pyrrolylthiones **10** and **11**, respectively (Scheme 2). Their NMR spectroscopic and analytical data are similar to those of **14** and allow for their formulation as *trans* square planar complexes with a ligand-to-metal ratio of 2:1. The purple thiobenzoylpyrrolato complex **14** was distinguished by a very low solubility in noncoordinating solvents, whereas the red thioacetyl analogue was freely soluble in a variety of solvents. The pronounced electronic influence of the methyl or phenyl group on the rest of the complex as compared to the pyrrolyl group in **14** is demonstrated by their significantly varying optical spectra, shown in Figure 4. Both spectra exhibit the same general pattern, with that of the phenyl-substituted complex **14** being ∼25 nm bathochromically shifted as compared to that of the methyl analogue **13**.

Steric Requirements of the 2-Pyrrolylthionato Moiety. In an attempt to prepare complexes of derivatized di-2-pyrrolyl thiones, hexamethylpyrrolylthione **9** was mixed with Ni(II) in the presence of base, as described above. To our surprise, not a trace of a nickel complex could be detected. Instead, the free ligand was recovered quantitatively. Due to the electronic similarity of the ligands, as judged by their similar optical spectra, electronic arguments do not seem adequate to explain these findings. The key to understanding the finding lies in the steric interaction of the α-substituents. On the basis of the X-ray crystal data of nickel complex **14**, a computer-generated model[42] in which the α-hydrogens of structure **14** had been replaced with methyl groups indicated a large overlap of the van der Waals radii of the α-methyl groups and the sulfur of the opposing ligand. This makes the achievement of a square planar, undistorted arrangement impossible. Interestingly, the formation of a tetrahedral complex, although sterically possible, was not observed either. The hypothesis that any complex formation is prevented by the bulk of an α-substituent is strengthened by the smooth complexation of Ni(II) by the α-unsubstituted β,β'-dimethyl thione **8** to give the corresponding square planar complex. Its analytical and spectroscopic properties all fall, as compared to those of **14**, within expectation.

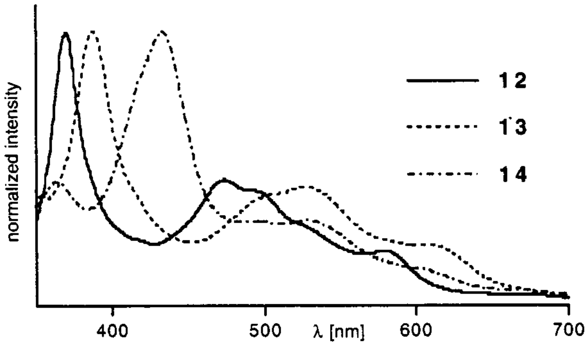


Figure 4. Normalized optical spectra (CH_2Cl_2) of bis(2-thioacetylpyrrolato)nickel(II) complex **12**, bis(2-thiobenzoylpyrrolato)nickel(II) complex **13**, and bis(2-pyrrolylthionato)nickel(II) complex **14**.

Reaction of Thione 6 with Hg(II). To evaluate the propensity of **6** to coordinate to other metals, it was reacted with Hg(II) and Co(II and III) (vide infra). Mercury was chosen for its known thiophilicity and its disposition to form tetrahedral complexes and to investigate the nature of the complex mentioned by Clezy.[22] The reaction of **6** with mercury(II) acetate in MeOH produced a fine, bright yellow crystalline precipitate, providing an elemental analysis indicating the composition $C_{18}H_{14}N_4HgS_2$, corresponding to complex **17** with a ligand-to-metal stoichiometry of 2:1. Its solubility in solvents such as acetone or methylene chloride was much lower as compared to that of the nickel complex **14**, and the optical spectrum of the bright yellow solution, shown in Figure 1, differed significantly as well. It is, devoid of dd transitions and CT bands, very much like that of the free ligand. The complex dissolves in DMSO at sufficient concentration for analysis by NMR spectroscopy. The pattern expected for one set of equivalent ligands was readily apparent. These results suggest the expected formation of a tetrahedral complex with two chelating ligands around the central metal. However, an oligo- or polymeric structure with bridging ligands of 2:1 ligand-to-metal stoichiometry could not be excluded; consequently single crystals were grown by allowing a dilute solution of **17** in CH_2Cl_2 to evaporate slowly, and their X-ray diffraction pattern was analyzed. Crystal data are listed in Table 1, and selected bond lengths are listed in Table 3. A stereoview of an ORTEP representation of the molecule is shown in Figure 5. The structural analysis showed the molecule as a distorted tetrahedral complex coordinating through one nitrogen and the sulfur with a dihedral angle of 62.1° between the planes defined by the mercury, the coordinated nitrogen, and the sulfur atom of the respective ligands. The intraligand bond lengths and bond angles are, with one exception, equivalent to those observed in the nickel complex. The two pyrrolic units of the ligands are not uniplanar but angled by about 40°, a value comparable to that of the free ligand (31.9°).[35] However, the conformations in both the free ligand and complex **17** may well be governed by crystal packing effects.

Reaction of Thione 6 with Co(II) and Co(III). Co(II), as its acetate, was reacted with thione **6** as described above. This caused rapid precipitation of a dark solid. Chromatography proved it to be a mixture of two orange low-polarity compounds (**18-*mer*** and **18-*fac***) in the ratio of ∼4:6 with very similar optical spectra. The electronic spectrum of **18-*mer*** is shown in Figure 1. Both compounds have identical mass spectra (M^+ =

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(42) CAChe 4.1, Molecular Modeling Package, MM3 force field, Oxford Molecular, Beaverton, OR, 1999.

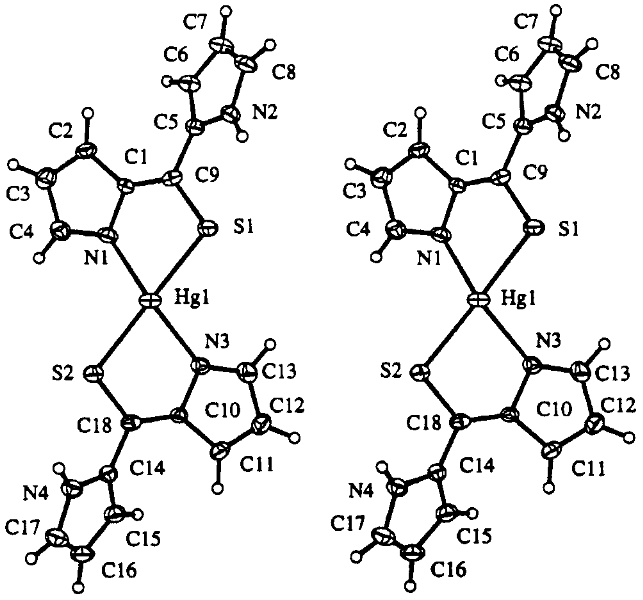

Figure 5. Stereoscopic view of the ORTEP representation (33% probability level) of the bis(2-pyrrolylthionato)mercury(II) complex **17**.

584) corresponding to a molecular formula of $C_{27}H_{21}N_6{}^{59}CoS_3$, i.e., to a complex with a ligand-to-metal stoichiometry of 3:1. The low polarity of the complexes indicates the presence of electroneutral complexes of Co(III). The facile aerial oxidation of Co(II) to Co(III) in the presence of amine ligands is well-known. Thus, all findings can be rationalized by the formation of (octahedral) Co(III) trischelates (diamagnetic, d^6 low spin). Complexes **18-*mer*** and **18-*fac*** also form by a ligand exchange reaction with Co(III)(acac)$_3$ and **6** in refluxing phenol. Unsymmetrical bidentate ligands forming octahedral complexes may form two stereoisomeric complexes.[43] These isomers, the *fac*- and the *mer*-isomers, can be, in case of the presence of kinetically inert Co(III) centers, separated by preparative thin-layer chromatography. Both isomers can be clearly distinguished by their differing symmetries as seen in their ^{1}H NMR spectra. The symmetry of the *fac*-isomer **18-*fac*** (point group C_3) bestows a C_3 axis onto the complex, rendering all three ligands equivalent. Consequently, the ^{1}H NMR spectrum of this isomer is very similar to that exhibited by the Ni(II) complex **14**. The *mer*-isomer **18-*mer*** contains no such high-symmetry element (point group C_1), and this renders all three ligands nonequivalent, reflected in its complex ^{1}H NMR spectrum. The final proof of the stereochemical assignment was provided by a single-crystal X-ray structure analysis of **18-*mer*** (as its acetone solvate), the ORTEP of which is shown in Figure 6. Selected bond lengths and angles are listed in Table 3. The donor atoms in the essentially planar ligands form an almost perfect octahedron around the central metal. All deviations in bond length as compared to those of the uncoordinated ligand are equivalent to those observed in the Ni(II) and the Hg(II) complexes **14** and **17**, respectively. The deviation of the pyrrolic units from coplanarity within the ligands average to 25°. The propensity of the NH protons to undergo hydrogen bonding is in this structure highlighted by the incorporation of one hydrogen-bonded molecule of acetone per complex into the crystal.

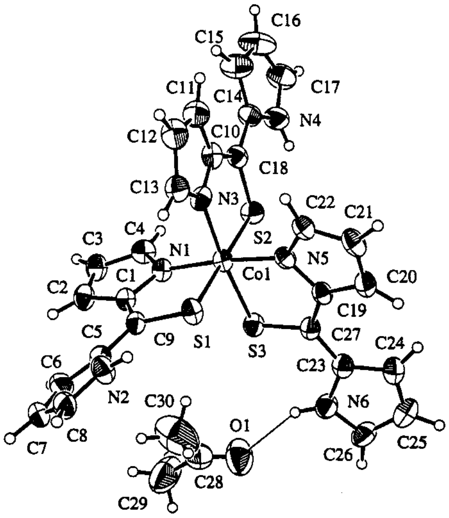

Figure 6. ORTEP representation (33% probability level) of the tris(2,2′-pyrrolylthionato)cobalt(III) complex **18-*mer*** (as its acetone solvate).

Conclusion

We have shown that 2-pyrrolylthiones can form stable coordinatively saturated metal complexes with Ni(II), Co(III), and Hg(II). As shown by a variety of spectroscopic methods and proven by single-crystal X-ray diffraction studies, the ligand serves in these complexes as a monoanionic bidentate N,S-donor. Depending on the metal, square planar, tetrahedral, or octahedral coordination spheres around the metal center can be achieved. α-Substituents other than hydrogen on the chelating moieties introduce too much steric interaction with an opposing sulfur atom upon chelation to the effect that no chelates for 5-methyl-substituted 2-pyrrolylpyrrole were observed.

This work expands the arsenal of known N,S-donor ligands by a class which is readily accessible in large quantities. Reports of the pharmacological activity of compounds containing the 2-pyrrolylthione and 2-indolylthione moieties have appeared in the literature;[25,44] however, their potential chelating ability was not recognized. In light of our findings it is interesting to consider the possible importance of metal coordination to the biological activity of these compounds.

Acknowledgment. We thank the Natural Sciences and Engineering Council (NSERC) of Canada for financial support.

Supporting Information Available: Details of the preparation for compounds **10** and **11** and detailed X-ray crystallographic files in CIF format for complexes **14**·0.28H$_2$O**,** **18-*mer***·Me$_2$CO**,** and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) von Zelewsky, A. *Stereochemistry of Coordination Compounds*; Wiley: New York, 1996.

(44) (a) Sato; Sunagawa *Chem. Pharm. Bull.* **1967**, *15*, 642. (b) Kost, A. N.; Gorbunova, S. M.; Basova, L. P.; Kiselev, V. K.; Gorbunov, V. I. *Pharm. Chem. J. (Engl. Transl.)* **1974**, *8*, 8. (c) Goerlitzer, K.; Hoelscher, D. *Arch. Pharm. (Weinheim, Ger.)* **1986**, *319*, 120.