Sodium 2-Methyl-2-propylthiolate, a Versatile Sulfur Reagent. Preparation of Protected Polysulfur Ligands and their Nickel(II) Complexes

JAN BECHER*, CARSTEN E. STIDSEN, HANS TOFTLUND and FAHMY M. ASAAD

Department of Chemistry, Odense University, DK-5230 Odense M, Denmark

(Received March 11, 1986; revised April 19, 1986)

Abstract

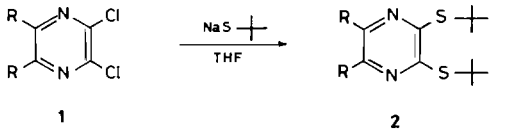
Multisulfur-containing ligands can conveniently be prepared by nucleophilic substitution of chlorine in various heterocyclic and other aromatic systems by the 2-methyl-2-propylthiolate anion, followed by elimination of isobutene from the resulting t-butylthioethers. The preparation of bis(3-thiolato-2(1H)-pyrazinethione)-nickelat(II) (**5a**) by this methodology is described.

Introduction

There is currently much interest in the preparation of multisulfur-containing compounds since the discovery of superconductivity in mixed valence perchlorates of tetrathiafulvalenes (TTF) and related compounds [1]. Metal complexes such as bis(4,5-dimercapto-1,3-dithiole-2-thion)-nickel(II) [2] give salts with TTF which show high conductivity. Furthermore, superconductivity has been reported in the compound $TTF(Ni(dmit)_2)_2$ [3]. We have recently prepared a variety of sulfur-containing ligands via their corresponding bis-t-butylthioethers [4]. The current interest in these types of sulfur compounds has prompted us to report that this methodology can also be used for the preparation of the new polysulfur ligand precursors **2a**–**2d**, as well as the new stable nickel(II) complexes **5a**, **6a**, and the 2,3-quinoxaline dithiolato complex **5c**, which has previously been reported by Theriot *et al.* [5]. For a review on 1,2-dithiolene complexes of transition metals, see ref. 11.

Results and Discussion

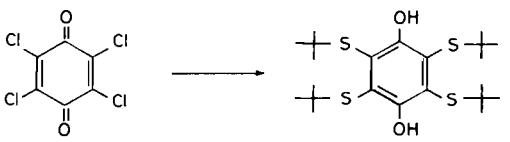
Thus, the 2,3-dichloropyrazines gave the bis-t-butylthioethers (**2a**–**2c**) with sodium-t-butylthiolate in dry THF:



1 **2**

1	R	2	R
a	H	a	H
b	C_6H_5	b	C_6H_5
c	$-(CH)_4-$	c	$-(CH)_4-$
d	Cl	d	$SC(CH_3)_3$

The tetrakis-t-butylthioether (**2d**) was also obtained in fair yield, while 2,3,5,6-tetrachloroquinone (**3**) gave the corresponding hydroquinone **4** again in excellent yield:

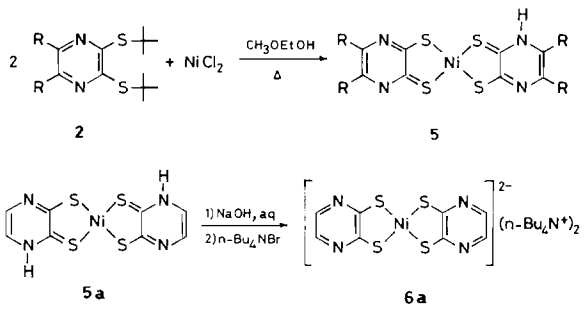


3 **4**

The mass spectra of the new t-butylthioethers all showed molecular ions of small abundance and relatively larger peaks due to the loss of the expected equivalents of isobutene. When 2,3-bis(2-methyl-2-propyl-thio)-pyrazine (**2a**) was refluxed with nickel(II) chloride containing traces of HCl in 2-methoxyethanol, isobutene was eliminated resulting in the precipitation of the dark blue nickel(II) complex **5a**. It is important to note that these reactions were all carried out under open atmosphere, reflecting the stability of the compounds towards oxidation under the reaction conditions used:

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50



Complex **5a** is insoluble in water and most organic solvents, but soluble in aqueous base. The red basic form can be transformed back to the blue acidic form by addition of hydrochloric acid. On addition of base complex **5a** yielded a soluble tetrabutylammonium salt **6a** which was recrystallized from ethylacetate as brown needles.

The electronic spectra of both the dark blue acidic forms **5a** and **5c** and the brown basic forms **6a** and **6c** agree quite well with the reported absorptions of **5c** and **6c** [5]. The square-planar, low-spin NiS_4 nature of these complexes is supported by the fact that the complexes are diamagnetic in the temperature range 5–293 K.

The tetradentate ligand precursors **2d** and **4** gave insoluble dark blue-black polymeric nickel(II) complexes with nickel(II) chloride [10]. The electrical properties of the mixed valence salts of these and related nickel(II) complexes are currently under investigation.

Experimental

Microanalyses were carried out at NOVO A/S, Copenhagen by Mr. Amsler or at University of Copenhagen by Mr. P. Hansen. ^1H and ^{13}C NMR spectra were determined on a Jeol FX 60Q, IR spectra on a Perkin-Elmer 580 spectrometer (KBr), UV spectra on a Varian CARY 210 spectrometer, MS spectra on a Varian MAT 311 A spectrometer. Magnetic susceptibility measurements were performed using the Faraday method. Melting points (uncorrected) were obtained on a Büchi apparatus. All preparations were carried out under open atmosphere, without exclusion of oxygen.

Preparation of Ligands, General Method

Sodium hydride (50% dispersion in oil, 2.2 equivalent per equivalent halogen) is suspended in dry tetrahydrofurane (50 ml). After cooling to 0 °C 2-methyl-2-propanethiole (2.2 equivalent per equivalent halogen) in dry tetrahydrofurane (5 ml) is added with stirring (15 min). After addition, the reaction mixture is stirred at room temperature for 1 h, whereupon the required di- or tetrachloro compound is added. Reaction time is as specified below. The reaction mixture is then added to water (200 ml, 0 °C) and worked up.

Method A

The precipitated crystals were filtered, washed with water, dried, and recrystallized as specified below.

Method B

No precipitation; extraction with ether (2 × 250 ml), drying (sodium sulfate), and concentration *in vacuo*. The semicrystalline residue was dissolved in hot n-hexane (50 ml) and left at 5 °C for 24 h. The crystals were filtered and washed with a little ice-cold n-hexane.

2,3-Bis(2-methyl-2-propylthio)-pyrazine (2a)

The starting 2,3-dichloropyrazine was prepared according to Adachi and Soto [6].

The general method gives after reflux for 3 h and work up by method B; **2a**, 2.45 g (96%), melting point (m.p.) 93–4 °C. UV(ethanol): λ_{max} (log ϵ): 231 (3.95), 272 (3.90), 336 (3.89). IR(KBr): 1360 (CH_3). MS: *m/e* (relative intensity %): 256(13), 200(7), 144(100), 57(32). ^1H NMR($CDCl_3$): δ = 1.61 (s, 18H, CH_3), 8.02 (s, 2H, pyrazine). ^{13}C NMR-($CDCl_3$): δ = 30.29 (CH_3), 49.29 (CMe_3), 137.3 (C-5, C-6), 155.8 (C-2, C-3). *Anal.* Calc. for $C_{12}H_{20}N_2S_2$ (256.43): C, 56.21; H, 7.86; N, 10.92. Found: C, 56.73; H, 8.12; N, 10.89%.

2,3-Bis(2-methyl-2-propylthio)-5,6-diphenyl-pyrazine (2b)

2,3-Dichloro-5,6-diphenylpyrazine was prepared according to Karmas and Spoerri [7].

The general method gives after 24 h at 20 °C and work up by method A; **2b**, 3.10 g (76%), m.p. 190–1 °C (ethanol). UV(ethanol): λ_{max} (log ϵ): 248 (4.30), 306 (4.15), 360 (4.15). IR(KBr): 1352 (CH_3). MS: *m/e* (relative intensity %): 408(21), 352(4), 296(100), 178(22), 57(44). ^1H NMR($CDCl_3$): δ = 1.67 (s, 18H, CH_3), 7.30 (m, 10H, phenyl). ^{13}C NMR($CDCl_3$): δ = 30.49 (CH_3), 49.39 (CMe_3), 128.0 (phenyl C-2 og C-4), 129.7 (phenyl C-3), 138.8 (phenyl C-1), 145.3 (pyrazine C-5 og C-6) 152.1 (pyrazine C-2 og C-3). *Anal.* Calc. for $C_{24}H_{28}N_2S_2$ (408.63): C, 70.54; H, 6.91; N, 6.86. Found: C, 70.44; H, 6.93; N, 6.75%.

2,3-Bis(2-methyl-2-propylthio)-quinoxaline (2c)

2,3-Dichloroquinoxalin was prepared according to Cheeseman [8].

The general method gives after 1 h at 20 °C and work up by method B; **2c**, 2.91 g (95%), m.p. 103–4 °C. UV(ethanol): λ_{max} (log ϵ): 222 (4.38), 268 (4.38), 355 (4.07), 373 (4.10). IR(KBr): 1362 (CH_3). MS: *m/e* (relative intensity %): 306(23), 250(9),

194(100), 150(8), 57(41). ^{1}H NMR($CDCl_3$): δ = 1.74 (s, 18H, CH_3), 7.65 (m, 4H, δ_A = 7.81, δ_B = 7.50, J_{AB} = 8.40 Hz, $J_{AB'}$ = 1.35 Hz, $J_{AA'}$ = 1.07 Hz, $J_{BB'}$ = 7.26 Hz, quinoxaline H5–H8). ^{13}C NMR-($CDCl_3$): δ = 30.02 (CH_3), 49.80 (CMe_3), 127.4 (C-6), 127.6 (C-5), 138.8 (C-4a), 155.6 (C-2). *Anal.* Calc. for $C_{16}H_{22}N_2S_2$ (306.49): C, 62.70; H, 7.24; N, 9.14. Found: C, 62.98; H, 7.31; N, 9.01%.

2,3,5,6-Tetrakis(2-methyl-2-propylthio)-pyrazine (2d)

Tetrachloropyrazine was prepared according to Allison *et al.* [9].

The general method gives after 24 h at 20 °C and work up by method A; **2d**, 3.12 g (72%), m.p. 211–2 °C (butanon). UV(ethanol): λ_{max} (log ϵ): 250 (4.04), 305 (4.12), 387 (3.98). IR(KBr): 1350 (CH_3). MS: *m/e* (relative intensity %): 432(18), 376(2), 320(7), 264(21), 208(63), 57(100). ^{1}H NMR($CDCl_3$): δ = 1.57 (s, CH_3). ^{13}C NMR($CDCl_3$): δ = 30.91 (CH_3), 48.97 (CMe_3), 150.8 (pyrazine C-2, C-3, C-5, and C-6). *Anal.* Calc. for $C_{20}H_{36}N_2S_4$ (432.78): C, 55.51; H, 8.38; N, 6.47. Found: C, 55.73; H, 8.57; N, 6.42%.

2,3,5,6-Tetrakis(2-methyl-2-propylthio)-1,4-dihydroxybenzene (4)

2,3,5,6-Tetrachloro-quinone (Chloranil) was obtained from Aldrich.

The general method gives after 1 h at −70 °C and 24 h at 20 °C, followed by work up by method A; **2e**, 3.89 g (84%), m.p. 198–9 °C (pet.ether). UV-(ethanol): λ_{max} (log ϵ): 222 (4.43), 240sh (4.19), 260sh (4.01), 361 (3.97), 372 (3.97). IR(KBr): 3270 br (OH), 1365 (CH_3). MS: *m/e* (relative intensity %): 462(20), 406(2), 350(16), 294(22), 238(50), 57(100). ^{1}H NMR($CDCl_3$): δ = 1.33 (s, 36H, CH_3), 7.75 (s, 2H, OH). ^{13}C NMR($CDCl_3$: δ = 31.45 (CH_3), 50.84 (CMe_3), 127.9 (C-2), 155.5 (C-1). *Anal.* Calc. for $C_{22}H_{38}O_2S_4$ (462.80): C, 57.10; H, 8.28. Found: C, 57.41; H, 8.40%.

Bis(3-thiolato-2(1H)-pyrazinethione)-nickelat(II) (5a)

Anhydrous nickel(II) chloride (0.260 g, 2 mmol), conc. hydrochloric acid (3 drops), and 2,3-bis(2-methyl-2-propylthio)-pyrazine (1.025 g, 4 mmol) is added to 2-methoxyethanol (50 ml). This mixture is refluxed for 3 h. Cooling and filtration of the precipitated 0.55 g (80%) of dark blue crystals of complex **5a**. The crude product was dissolved in sodium hydroxide (1 M, 50 ml) and the aqueous phase washed with ether. Complex **5a** was reprecipitated by addition of hydrochloric acid (1 M), filtered, and dried *in vacuo* (50 °C, 24 h) to give 0.52 g (76%), m.p. > 260 °C. UV(DMF): λ_{max} (log ϵ): pH < 7: 304 (4.47), 346 (4.27), 475 (3.57), 578 (3.92); pH > 7: 304 (4.66), 479 (3.94), 506 (3.87). IR(KBr): 3450, 3100 (NH, amid), 2600br. (S^-), 1040 (C=S), 1080 (C=S), 503 (Ni–S), 325 (Ni–S). *Anal.* Calc. for $C_8H_6N_4NiS_4$ (345.13): C, 27.84; H, 1.75; N, 16.23. Found: C, 27.50; H, 1.81; N, 16.06%.

Bis(3-thiolato-2(1H)-quinoxalinethione)-nickelat(II) (5c)

The general method described for complex **5a** was used. Thus, anhydrous nickel(II) chloride (0.130 g, 1 mmol), conc. hydrochloric acid (1 drop) and 2,3-bis(2-methyl-2-propylthio)-quinoxaline (0.618 g, 2 mmol) was refluxed in 2-methoxyethanol (100 ml) for 12 h. Cooling and filtration yielded 0.345 g (78%) of dark blue crystals of complex **5c**, m.p. > 260 °C/ abs. ethanol. ($C_{16}H_{10}N_4NiS_4$, 445.2), see ref. 5. UV(DMF): λ_{max} (log ϵ): pH < 7: 305 (4.65); 355 (4.30), 373 (4.34), 599 (4.20), 655 (4.16); pH > 7: 314 (4.82), 344 (4.37), 355 (4.31), 532 (4.25), 561 (4.27).

Bis(tetrabutylammonium)-bis(2,3-dithiolato-pyrazine)-nickelat(II) (6a)

Bis(3-thiolato-2(1*H*)-pyrazinethione)-nickelat(II), (0.5 g, 1.4 mmol) was dissolved in sodium hydroxide (0.1 M, 30 ml), tetrabutylammonium bromide (0.97 g, 3 mmol) was added and the mixture extracted with methylenchloride (2 × 100 ml). The organic phase was washed with water and dried (sodium sulfate). Concentration *in vacuo* yielded an oil which was triturated with hot ethylacetate. The precipitated brown needles of salt **6a** were isolated to give 1.40 g (95%), m.p. 172–4 °C. ^{1}H NMR($CDCl_3$): δ = 0.93 (m, 24H, CH_3), 1.2–1.9 (m, 32H, CH_2), 3.43 (m, 16H, $N-CH_2$), 7.93 (s, 4H, pyrazine). *Anal.* Calc. for $C_{40}H_{76}N_6NiS_4$ (828.04): C, 58.02; H, 9.25; N, 10.15. Found: C, 57.66; H, 9.24; N, 9.95%.

Acknowledgement

A postdoctoral grant from DANIDA, Denmark, to F.M.A. is gratefully acknowledged.

References

1 (a) S. S. P. Parkin, E. M. Engler, Schumaker, R. Lagie, V. Y. Lee, J. C. Scott and R. L. Greene, *Phys. Rev. Lett., 50,* 270 (1983); (b) A. J. Epstein and E. M. Conwell (eds.), *Mol. Cryst. Liq. Cryst., 79* (1982); (c) K. Bechgaard, K. Carneiro, F. B. Rasmussen and M. Olsen, *J. Am. Chem. Soc., 103,* 2440 (1981); (d) K. Bechgaard, K. Carneiro, M. Olsen, F. B. Rasmussen and C. S. Jacobsen, *Phys. Rev. Lett., 46,* 852 (1981); (e) D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett. (Paris), 41,* L95 (1980); (f) L. Brossard, M. Ribault, L. Valade and P. Cassoux, *C.R. Acad. Sci. Paris, 320,* S.II, 205 (1986).

2 L. Valade, M. Bousseau, A. Gleizes and P. Cassoux, *J. Chem. Soc., Chem. Commun.,* 110 (1983).

3 M. Bousseau, L. Valade, M.-F. Bruniquel, P. Cassoux, M. Garbauskas, L. Interrante and J. Kasper, *Nouv. J. Chim., 8,* 3 (1984).
4 J. Becher, H. Toftlund and P. H. Olesen, *J. Chem. Soc., Chem. Commun.,* 741 (1983); (b) J. Becher, H. Toftlund, P. H. Olesen and H. Nissen, *Inorg. Chim. Acta, 103,* 167 (1985).
5 L. J. Theriot, K. K. Ganguli, S. Kavarnos and I. Bernal, *J. Inorg. Nucl. Chem., 31,* 3133 (1969).
6 J. Adachi and N. Sato, *J. Org. Chem., 37,* 221 (1972).
7 G. Karmas and P. E. Spoerri, *J. Am. Chem. Soc., 78,* 4071 (1956).
8 G. W. H. Cheeseman, *J. Chem. Soc.,* 1804 (1955).
9 C. G. Allison, R. D. Chambers, J. A. H. MacBridge and W. K. R. Musgrave, *J. Chem. Soc. C,* 1023 (1970).
10 J. Becher and C. Stidsen, unpublished results.
11 R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem., 22,* 303 (1979).