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Nickel–Thiolate Chemistry Based on Chelating Ligands: Controlling the Course of Self-Assembly Reactions via Ligand Bite Distances. Synthesis, Structures, and Properties of the Homoleptic Complexes $[Ni_3(SCH_2C_6H_4CH_2S)_4]^{2-}$, $[Ni_3(SCH_2CH_2S)_4]^{2-}$, and $[Ni_6(SCH_2CH_2CH_2S)_7]^{2-}$

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The reaction systems $NiCl_2/Na_2$(dithiolate) in methanol (dithiolate = S_2-*o*-xyl^{2-}, edt^{2-}) and acetone (dithiolate = pdt^{2-}) afford the trinuclear and hexanuclear complexes $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ (**1**, S_2-*o*-xyl^{2-} = *o*-xylene-α,α'-dithiolate), $[Ni_3(edt)_4]^{2-}$ (**2**, edt^{2-} = 1,2-ethanedithiolate), and $[Ni_6(pdt)_7]^{2-}$ (**3**, pdt^{2-} = 1,3-propanedithiolate), which were isolated as their Et_4N^+ or Ph_4P^+ salts. $[Et_4N]_2[Ni_3(S_2\text{-}o\text{-xyl})_4]\cdot 2MeOH$ (**4**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.131$ (3) Å, $b = 15.148$ (4) Å, $c = 16.694$ (4) Å, $\alpha = 110.26$ (3)°, $\beta = 99.41$ (3)°, $\gamma = 110.25$ (3)°, and $Z = 2$. The refinement converged to $R = 0.058$. $[Ph_4P]_2[Ni_3(edt)_4]$ (**5**) crystallizes in the triclinic space group $P\bar{1}$ with $a = 9.974$ (3) Å, $b = 11.303$ (4) Å, $c = 13.840$ (5) Å, $\alpha = 105.91$ (3)°, $\beta = 98.91$ (3)°, $\gamma = 112.62$ (2)°, and $Z = 1$. The structure was refined to $R = 0.038$. **1** may be seen as arising from the chelation of two identical $[Ni(S_2\text{-}o\text{-xyl})]$ entities to a $[Ni(S_2\text{-}o\text{-xyl})_2]^{2-}$ anion; **2** arises from the chelation of two $[Ni(edt)_2]^{2-}$ anions to a third Ni^{2+} cation in such a manner that the central Ni(II) is surrounded by four coplanar bridging sulfur atoms. The different appearance of the structures of **1** and **2** is necessitated by the steric requirements of the chelating S_2-*o*-xyl^{2-} and edt^{2-} ligands, respectively. The resulting Ni_3S_8 entities ideally have a boat (**1**) and a chair (**2**) conformation. $[Et_4N]_2[Ni_6(pdt)_7]$ (**6**) crystallizes in the orthorhombic space group *Pnma* with $a = 35.487$ (9) Å, $b = 17.023$ (4) Å, $c = 9.284$ (3) Å, and $Z = 4$. The structure was refined to $R = 0.067$. **3** can be viewed as consisting of two $[Ni_3(pdt)_4]^{2-}$ subunits with structures analogous to **1** sharing a common pdt^{2-} ligand.

Introduction

The chemistry of the metal thiolates has been developed extensively in recent years and has reached almost a stage comparable to that of the metal alkoxides.[1] The research in the last decade has resulted in a broad class of compounds with an astounding degree of complexity and nuclearity.[2]

One increasing subgroup among these metal thiolates are those of the platinum group metals. Structurally known examples include the mononuclear anions $[Ni(SR)_4]^{2-}$,[3] the neutral cyclic $[Ni_n(SR)_{2n}]$ molecules (n = 4, 5, 6, 8),[4] and the acyclic species $[Ni_n(SR)_{2n+2}]^{2-}$ (n = 2, 3)[5a–c] for nickel. Except for the mononuclear nickel thiolate species, all compounds contain essentially diamagnetic square-planar NiS_4 units, and the structures of all polynuclear compounds can be generated by edge-linking of these structural motifs. One interesting aspect stimulating the exploration of metal thiolate chemistry is given by the molecular–condensed state analogy. If one focuses at extended lattices containing no discrete clusters, some harbingers giving evidence for the persistence of structural units in molecular and solid state systems are provided by $[(MeCp)_2V_2S_4]$[6] and $[V_2(\mu\text{-}S_2)_2(i\text{-}Bu_2NCS_2)_4]$,[7] $[Fe_3S_4(SR)_4]^{3-}$,[8] $[Pd_n(SR)_{2n+2}]^{2-}$,[5d,e] and $[Ni_n(SR)_{2n+2}]^{2-}$,[5a–c] $[Ni_n(SR)_{2n}]$,[4] and $[Pd_6(SR)_{12}]$[9] or $[Zn_{10}S_4(SR)_{16}]^{4-}$,[10] whose metal–sulfur cores represent small solubilized portions of the inorganic solids patronite $V(S_2)_2$[11] and erdite $NaFeS_2\cdot 2H_2O$,[12] M^IFeS_2,[13] M^IPtS_2,[14] $M^I_2Pd_3S_4$,[15] or ZnS and $M^I_2ZnS_2$.[16] Although we can find a considerable amount of structural and related data for molecular complexes, there exists a plethora of sulfide minerals and synthetic phases[17] with a variety of structures not yet encountered in discrete molecular units. Still another incentive for the development of a systematic nickel

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thiolate chemistry has been the discovery of nickel centers in certain hydrogenases.[18] Recent EXAFS studies are consistent with a dominant Ni–S ligation of the nickel centers.

In the search for novel nickel thiolate complexes (as well as metal thiolate complexes in general), we and others[19–32] have employed potentially chelating dithiolate ligands. By means of their S···S bite distances, these ligands have been used successfully in controlling the product distribution in self-assembly reactions of metal thiolate species. Whereas the S_2-*o*-xyl^{2-} ligand preferentially supports a tetrahedral stereochemistry, the edt^{2-} ligand fits perfectly well into a square-planar NiS_4 unit, but does not allow an undistorted tetrahedral coordination.[19f–h,21] The pdt^{2-} ligand can be assumed to be intermediate between S_2-*o*-xyl^{2-} and edt^{2-}.

Recent investigations on nickel(II) systems[3d,5c,29,32] together with earlier demonstrations for a number of Mn(II), Fe(II,III) and Co(II) systems[21,27–29] suggest that a variety of new structural types of metal–(sulfide)–thiolate species can be obtained by appropriate variation of the chelating ligand. The matter has been pursued here by exploring the reaction systems Ni(II)/X/Y (X = S_2-*o*-xyl^{2-}, pdt^{2-}, edt^{2-}; Y = S^{2-}, $S_2{}^{2-}$, $S_x{}^{2-}$ ($x > 2$), S_8, SR^-) and the synthesis and structural determination of four complexes, **1**, **2**, **3**, and $[Ni_4(S_2)(edt)_4]^{2-}$ (**7**), the latter one being one rare example of a complex simultaneously containing both disulfide and thiolate ligands.[25,32] We have briefly described a part of our initial results in relation to the above question.[28,32] Here we report a more complete set of results including full synthetic and structural details. The synthesis and structure of **7** is given in the following paper in this issue.

Experimental Section

Preparation of Compounds. All preparations were performed in gloveboxes under an atmosphere of pure dinitrogen. H_2edt and H_2pdt were procured from Jansen Chimica. $NiCl_2$ was purchased from Merck-Schuchardt. Solvents were degassed prior to use. H_2S_2-*o*-xyl was synthesized by a standard procedure.[31c] Na_2pdt was prepared from the dithiole and a solution of sodium in absolute ethanol and precipitated by addition of diethyl ether in small portions to the solution. The product was collected by filtration, washed thoroughly with ether, dried in vacuo, and stored under anaerobic conditions. Na_2S_2-*o*-xyl was obtained as a white powder and used in the following preparations unless generated in situ. Chemical analyses were performed by the microanalytical laboratories of Beller, Göttingen, FRG, and in the Institute of Organic Chemistry at the University of Münster.

$[Et_4N]_2[Ni_3(S_2$-*o*-xyl$)_4]\cdot 2MeOH$ (4) was initially obtained by the following procedure: A suspension of $NiCl_2$ (3.89 g, 30 mmol) in 50 mL of methanol was treated with a solution of sodium (1.38 g, 60 mmol) and H_2S_2-*o*-xyl (5.11 g, 30 mmol) in 60 mL of methanol. When the initial precipitate was treated with a solution of sodium (0.69 g, 30 mmol) and benzenethiolate (3.1 mL, 30 mmol) in 40 mL of methanol, a brown solution was obtained. The mixture was stirred for 2 h and filtered. Upon addition of Et_4NCl (4.97 g, 30 mmol), dark brown crystals of **4** separated in a course of 2 days. The product was recrystallized from DMF/methanol (1:1). Yield: 2.7 g (23%).

A more rational synthetic procedure is as follows: a suspension of $NiCl_2$ (2.59 g, 20 mmol) in 40 mL of methanol was treated with a solution of sodium (2.07 g, 90 mmol) and H_2S_2-*o*-xyl (7.66 g, 45 mmol) in 70 mL of methanol. The color rapidly turned to a dark brown. The mixture was stirred for 2 h and filtered. NEt_4Cl (3.31 g, 20 mmol) was added, and the solution was stored at −25 °C for 2 days. Under these conditions, a precipitate is formed. The material was collected by filtration and dissolved in a minimum of warm (ca. 75 °C) DMF, and methanol was added until incipient crystallization. After the solution was cooled to −30 °C, a crop of dark brown crystals was obtained after 3 days, collected by filtration, and dried in vacuo. Combined yield: 58 g (78%).

Anal. Calcd for $C_{50}H_{80}N_2O_2Ni_3S_8$: C, 51.16; H, 6.87; N, 2.37; Ni, 15.60; S, 21.85. Found: C, 51.00; H, 6.87; N, 2.18; Ni, 15.17; S, 22.08.

$[Et_4N]_2[Ni_6(pdt)_7]$ (6) was synthesized by the following procedure: To a mixture of solid Na_2pdt (1.98 g, 13 mmol) and $NiCl_2$ (1.30 g, 10 mmol) was added 80 mL of acetone. The solution turned brown-green slowly. After being stirred for 20 h at ambient temperature, the reaction mixture was filtered and NEt_4BF_4 (1.2 g, 5.5 mmol) was added. After 2 days black crystals of **6** developed from the dark green solution. They were collected by filtration, washed with ether, and dried in vacuo (yield: 1.02 g (48.3%)).

Anal. Calcd for $C_{37}H_{82}N_2Ni_6S_{14}$: C, 32.77; H, 6.09; N, 2.07. Found: C, 31.98; H, 5.90; N, 2.18.

$[Ph_4P]_2[Ni_3(edt)_4]$ (5). A solution of sodium (1.38 g, 60 mmol) and H_2edt (2.5 mL, 30 mmol) in 50 mL of methanol was added to a suspension of $NiCl_2$ (2.59 g, 20 mmol) in 40 mL of methanol. The green solution was stirred for 2 h and filtered onto Ph_4PBr (4.67 g, 10 mmol). The solution was stored at −30 °C for 2 days. During that time dark green crystals of **5** separated from the solution. The product was collected by filtration and recrystallized from DMF/MeOH (ca. 75 °C) to afford 3.2 g (52% yield) of dark green crystalline material.

Anal. Calcd for $C_{56}H_{56}Ni_3P_2S_8$: C, 54.97; H, 4.61; Ni, 14.39; P, 5.06; S, 20.96. Found: C, 54.48; H, 4.85; Ni, 13.74; P, 4.91; S, 21.49.

Collection and Reduction of X-ray Data. Crystals of **4–6** were obtained from the reaction mixtures. The corresponding quaternary am-

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Table I. Details of Data Collection and Structure Refinements for $[Et_4N]_2[Ni_3(S_2\text{-}o\text{-xyl})_4]\cdot 2MeOH$ (**4**), $[Et_4N]_2[Ni_6(pdt)_7]$ (**6**), and $[Ph_4P]_2[Ni_3(edt)_4]$ (**5**)

	4	**6**	**5**
formula	$C_{50}H_{80}N_2O_2Ni_3Si_8$	$C_{37}H_{82}N_2Ni_6S_{14}$	$C_{56}H_{56}Ni_3P_2S_8$
mol wt	1173.85	1356.18	1223.56
a, Å	13.131 (3)	35.487 (9)	9.974 (3)
b, Å	15.148 (4)	17.023 (4)	11.303 (4)
c, Å	16.694 (4)	9.284 (3)	13.840 (5)
α, deg	110.26 (3)		105.91 (3)
β, deg	99.41 (3)		98.91 (3)
γ, deg	110.25 (3)		112.62 (2)
V, Å^3	2767.0	5608.41	1324.13
cryst syst	triclinic	orthorhombic	triclinic
Z	2	4	1
d_{calc}, g cm^{-3}	1.41	1.61	1.54
space group	$P\bar{1}$	*Pnma*	$P\bar{1}$
cryst dimens	0.3 × 0.3 × 0.2	0.3 × 0.15 × 0.2	0.3 × 0.2 × 0.2
μ, cm^{-1} (Mo Kα)	13.4	24.9	14.6
temp, K	143	150	150
scan speed, deg/min	4–29	2–29	4–29
bkgd/scan-ratio	0.5	1.0	0.5
scan mode	$\theta/2\theta$ scan	ω scan	$\theta/2\theta$ scan
scan range, deg	$2(\Delta\theta)$ + Kα splitting	$1(\Delta\omega)$	$2(\Delta\theta)$ + Kα splitting
$2\theta_{max}$, deg	48	54	54
no. of unique data calcd	8497 $(+h,\pm k,\pm l)$	6244 $(+h,+k,+l)$	5784 $(+h,\pm k,\pm l)$
no. of obsd data ($I \geq 1.96\ \sigma(I)$)	6777	3443	4531
no. of variables	586	264	313
R/R_w	0.058/0.059	0.067/0.062	0.038/0.039

monium and phosphonium salts used for precipitation were pressed into pellets, and the reaction solutions were carefully filtered onto the pellets. The solutions were allowed to stand without moving for 2 or 3 days at ambient temperature. During that time crystals developed suitable for X-ray diffraction.

Single crystals selected for data collection each were fixed with a trace of silicone grease at the top of a glass capillary and cooled to approximately 150 K under a stream of cold nitrogen gas by using a modified Syntex LT-1 low-temperature device. X-ray diffraction data were collected on an automated Syntex P2$_1$ four-circle diffractometer equipped with a Mo Kα source, a graphite monochromator, and a scintillation counter. The unit cell dimensions and their standard deviations were obtained by a least-squares fit of the setting angles of at least 15 centered reflections in the range 25° < 2θ < 30°. Data were collected in the $\theta/2\theta$ scan mode for **4** and **5** and in the ω scan mode for **6**. The intensity of one standard reflection measured every 99 scans did not show any significant changes during the data collection. The intensity profiles of all reflections indicated stable crystal settings during the measurements. All calculations were done by using the programs of the EXTL[33] and SHELXTL[34] program packages. Data reduction was done by applying Lorentz and polarization corrections.[35] Empirical absorption corrections (ψ scan) were applied. Further details relevant to the data collections and structure refinements are collected in Table I and ref 36–38.

Solution and Refinement of the Structures. The calculations were performed on a Data General ECLIPSE S/200 minicomputer. All structures were solved by direct methods (MULTAN[37] and X[34]), which revealed the positions of the metal atom and some of the sulfur atoms. The remaining non-hydrogen atom positions were located from difference Fourier maps computed after least-squares refinement cycles. Atomic scattering factors for spherical neutral free atoms (bonded for hydrogen) were taken from standard sources.[38] Both the f' and f'' components of the anomalous dispersion[38] were included for all non-hydrogen atoms. Unless stated otherwise, all non-hydrogen atoms were refined anisotropically during the last stage of the refinement. Calculated fixed contributions from the hydrogen atoms (d(C–H) = 0.96 Å) with isotropic thermal parameters set at 1.2 times the isotropic equivalent of the bonded

Table II. $[Et_4N]_2[Ni_3(S_2\text{-}o\text{-xyl})_4]\cdot 2MeOH$: Atomic Coordinates of the $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ Anion without H Atoms

atom	*x*	*y*	*z*
Ni(1)	0.62441 (6)	0.26692 (6)	0.44955 (5)
Ni(2)	0.37978 (6)	0.18482 (6)	0.31612 (5)
Ni(3)	0.22367 (7)	−0.02491 (6)	0.16002 (5)
S(1)	0.78285 (13)	0.30842 (12)	0.41547 (10)
S(2)	0.65550 (13)	0.21544 (13)	0.55392 (11)
S(3)	0.54866 (13)	0.31374 (12)	0.35091 (10)
S(4)	0.29894 (14)	0.13695 (12)	0.17284 (10)
S(5)	0.27924 (16)	−0.07842 (13)	0.04315 (12)
S(6)	0.13662 (15)	−0.16961 (12)	0.17234 (11)
S(7)	0.20371 (13)	0.06986 (12)	0.28715 (10)
S(8)	0.45316 (13)	0.24855 (12)	0.46279 (10)
C(1)	0.9119 (5)	0.3106 (5)	0.4807 (4)
C(2)	0.7908 (5)	0.2058 (5)	0.5800 (4)
C(3)	0.9486 (5)	0.3623 (4)	0.5810 (4)
C(4)	1.0416 (5)	0.4609 (5)	0.6294 (4)
C(5)	1.0816 (5)	0.5059 (5)	0.7224 (4)
C(6)	1.0305 (5)	0.4545 (5)	0.7700 (4)
C(7)	0.9363 (5)	0.3577 (5)	0.7223 (4)
C(8)	0.8949 (5)	0.3109 (4)	0.6283 (4)
C(9)	0.6099 (5)	0.3137 (5)	0.2600 (4)
C(10)	0.3944 (6)	0.1619 (5)	0.1064 (4)
C(11)	0.5494 (5)	0.3482 (5)	0.2011 (4)
C(12)	0.5926 (6)	0.4533 (5)	0.2191 (4)
C(13)	0.5396 (6)	0.4885 (5)	0.1679 (5)
C(14)	0.4399 (6)	0.4186 (6)	0.0961 (5)
C(15)	0.3958 (6)	0.3136 (5)	0.0772 (5)
C(16)	0.4480 (5)	0.2769 (5)	0.1285 (4)
C(17)	0.1937 (6)	−0.2138 (5)	−0.0427 (4)
C(18)	0.0620 (5)	−0.2882 (5)	0.0657 (4)
C(19)	0.2043 (5)	−0.2961 (5)	−0.0177 (4)
C(20)	0.2792 (6)	−0.3396 (5)	−0.0452 (4)
C(21)	0.2857 (6)	−0.4207 (6)	−0.0281 (5)
C(22)	0.2199 (6)	−0.4601 (5)	0.0185 (4)
C(23)	0.1471 (6)	−0.4159 (5)	0.0482 (4)
C(24)	0.1398 (5)	−0.3346 (5)	0.0308 (4)
C(25)	0.1868 (5)	0.0120 (5)	0.3663 (4)
C(26)	0.3965 (5)	0.1694 (5)	0.5203 (4)
C(27)	0.1818 (5)	0.0867 (4)	0.4511 (4)
C(28)	0.0754 (5)	0.0825 (5)	0.4574 (4)
C(29)	0.0672 (6)	0.1525 (5)	0.5322 (5)
C(30)	0.1651 (6)	0.2282 (5)	0.6031 (5)
C(31)	0.2696 (6)	0.2326 (5)	0.5978 (4)
C(32)	0.2797 (5)	0.1617 (5)	0.5232 (4)

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(33) Sparks, R. In *Computational Needs and Resources in Crystallography*; National Academy of Sciences: Washington, DC, 1973; pp 66–75.

(34) SHELXTL program package, Nicolet XRD Corp. Madison, WI.

(35) The data reduction formula is $F_o^2 = I/Lp$. I is defined as $[S - (B_1 + B_2)(t_s/2t_B)]\cdot s$, where S and B_1 and B_2 are the scan and individual background counts, respectively, t_S and t_B are their counting times, and s is the scan speed for the reflection. The variance of I was calculated as $\sigma(I)^2 = [S + (B_1 + B_2)(t_s/2t_B)^2]\cdot s$, the variance of F_o was defined according to $\sigma(F_o) = \sigma(I)/(2|F_o|Lp)$.

(36) The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = [\sigma^2(F_o) + (0.01|F_o|)^2]^{-1}$. The R factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(37) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect A: Cryst. Phys., Diffr., Gen. Theor. Crystallogr.* **1971**, *A27*, 368.

(38) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

Table III. $[Et_4N]_2[Ni_3(S_2\text{-}o\text{-xyl})_4]\cdot 2MeOH$: Selected Distances and Angles of the $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ Anion

	Distances (Å)		
Ni(1)–Ni(2)	3.131 (1)	Ni(1)–S(1)	2.185 (2)
Ni(2)–Ni(3)	3.016 (1)	Ni(1)–S(2)	2.177 (2)
S(1)···S(2)	3.465 (3)	Ni(1)–S(3)	2.228 (2)
S(1)···S(3)	3.126 (3)	Ni(1)–S(8)	2.226 (2)
S(3)···S(4)	3.461 (2)	Ni(2)–S(3)	2.206 (2)
S(3)···S(8)	2.687 (2)	Ni(2)–S(4)	2.193 (2)
S(4)···S(5)	3.121 (3)	Ni(2)–S(7)	2.208 (2)
S(4)···S(7)	2.735 (2)	Ni(2)–S(8)	2.192 (2)
S(5)···S(6)	3.415 (3)	Ni(3)–S(4)	2.219 (2)
S(6)···S(7)	3.167 (3)	Ni(3)–S(5)	2.185 (2)
S(7)···S(8)	3.446 (2)	Ni(3)–S(6)	2.193 (2)
S(8)···S(2)	3.123 (3)	Ni(3)–S(7)	2.229 (2)
	Angles (deg)		
Ni(1)–Ni(2)–Ni(3)	131.34 (4)	S(7)–Ni(2)–S(8)	103.13 (7)
S(1)–Ni(1)–S(2)	105.19 (8)	S(4)–Ni(3)–S(5)	90.23 (8)
S(1)–Ni(1)–S(3)	90.18 (7)	S(4)–Ni(3)–S(6)	167.23 (8)
S(1)–Ni(1)–S(8)	164.01 (8)	S(4)–Ni(3)–S(7)	75.90 (7)
S(2)–Ni(1)–S(3)	164.57 (8)	S(5)–Ni(3)–S(6)	102.51 (8)
S(2)–Ni(1)–S(8)	90.35 (7)	S(5)–Ni(3)–S(7)	164.95 (8)
S(3)–Ni(1)–S(8)	74.22 (7)	S(6)–Ni(3)–S(7)	91.49 (7)
S(3)–Ni(2)–S(4)	103.80 (7)	Ni(1)–S(3)–Ni(2)	89.84 (7)
S(3)–Ni(2)–S(7)	173.34 (8)	Ni(2)–S(4)–Ni(3)	86.26 (7)
S(3)–Ni(2)–S(8)	75.35 (7)	Ni(2)–S(7)–Ni(3)	85.66 (7)
S(4)–Ni(2)–S(7)	76.85 (7)	Ni(1)–S(8)–Ni(2)	90.26 (7)
S(4)–Ni(2)–S(8)	172.64 (8)		

carbon atom were included in the final refinement cycles.[36] The individual structure refinements are briefly described.

$[Et_4N]_2[Ni_3(S_2\text{-}o\text{-xyl})_4]\cdot 2MeOH$. Under the given Laue symmetry ($\bar{1}$), the distribution of normalized structure factors indicated the centrosymmetric space group $P\bar{1}$. The successful structure solution and refinement confirmed this choice. The asymmetric unit contains one anion, two cations, and two solvate molecules, all of which were well-behaved during the refinements. All hydrogen atoms could be located from a difference Fourier map. Their positional parameters were refined with isotropic thermal parameters being fixed at 4 Å^2. Final R factors and other details are included in Table I. Positional parameters of the anion are listed in Table II; selected interatomic distances and angles of the anion are compiled in Table III. Thermal parameters of the anion, atomic parameters of the cations and solvate molecules, and a complete list of distances and angles within the anions, cations, and solvate molecules as well as observed and calculated structure factors are provided in Tables S-I, S-IV, S-VII, and S-X (supplementary material).

$[Et_4N]_2[Ni_6(pdt)_7]$. Under the given Laue symmetry (mmm) the systematic absences ($0kl$, $k + l = 2n$, and $hk0$, $h = 2n$) are consistent with both orthorhombic space groups *Pnma* and $Pn2_1a$ (nonstandard setting of $Pna2_1$). The structure was solved by combined applications of direct-method and heavy-atom techniques and successfully refined in the space group *Pnma*. The asymmetric unit consists of one half-anion and two half-cations. The anion is situated on a crystallographic mirror plane.

After the refinement of the initial structural model, the thermal parameters indicated a conformational disorder of the terminal pdt^{2-} ligands of the anion. Attempts to model the disorder in terms of fractional site occupancies of the carbon atoms were unsuccessful. By symmetry, the central carbon atom of one propylene chain exhibits positional disorder across the crystallographic mirror plane, which in the refinements could be successfully taken into account with an occupancy of 50% for the two positions of the affected atom. As for the anion, each of the Et_4N^+ cations is situated on a crystallographic mirror plane. One of them exhibits a disorder of the methylene carbon atoms. The disorder was modeled successfully in terms of two sites with 50% occupancy for each of the affected atoms.

Refinements were carried out with isotropic temperature factors for the disordered non-hydrogen atoms. In these cases, the contributions of the bonded hydrogen atoms were neglected. Final R factors and other details are listed in Table I, positional parameters of the anion are listed in Table IV; interatomic distances and angles within the Ni–S frame of the anion are compiled in Table V. Thermal parameters for the anion, atomic parameters of the cations, and a complete list of distances and angles within the anions and cations as well as structure factor tables are given in Tables S-II, S-V, S-VIII, and S-XI, respectively (supplementary material).

$[Ph_4P]_2[Ni_3(edt)_4]$ Under the given Laue symmetry ($\bar{1}$) the distribution of normalized structure factors indicated a centrosymmetric crystal lattice. Assuming the space group $P\bar{1}$, the structure was successfully solved and refined. The asymmetric unit contains one half-anion and one cation, all of which were well-behaved during the refinement. Final R factors and other details are given in Table I, positional parameters of the anion are provided in Table VI, and distances and angles of the anion are compiled in Table VII. Thermal parameters for the anion, atomic parameters of the cations, and a complete list of distances and angles within the anions and cations as well as structure factor tables are given in Tables S-III, S-VII, S-IX, and S-XII (supplementary material).

Other Physical Measurements. All samples were prepared and measured under anaerobic conditions. Absorption spectra were obtained with a Perkin-Elmer 551S spectrophotometer. Solid-state magnetic susceptibilities of 4–6 and $[Ph_4P]_2[Ni_4(S_2)(edt)_4]\cdot MeOH$ were determined at three different temperatures (293, 195, and 90 K) and different magnetic

Table IV. $[Et_4N]_2[Ni_6(pdt)_7]$: Atomic Coordinates of the $[Ni_6(pdt)_7]^{2-}$ Anion without H Atoms

atom	*x*	*y*	*z*
Ni(1)	0.07827 (3)	0.16648 (6)	0.78102 (12)
Ni(2)	0.08111 (3)	0.00510 (6)	0.78962 (12)
Ni(3)	0.14801 (3)	–0.03203 (7)	0.93924 (13)
S(1)	0.07616 (6)	0.0821 (1)	0.6012 (2)
S(2)	0.03566 (5)	0.0830 (1)	0.8595 (2)
S(3)	0.07574 (9)	0.25	0.9595 (4)
S(4)	0.11812 (9)	0.25	0.6868 (4)
S(5)	0.12799 (6)	–0.0700 (1)	0.7229 (3)
S(6)	0.08808 (6)	–0.0685 (1)	0.9792 (3)
S(7)	0.20313 (7)	–0.0015 (2)	0.8576 (3)
S(8)	0.15854 (8)	–0.0078 (3)	1.1632 (3)
C(1)	0.1182 (2)	0.0870 (5)	0.4893 (9)
C(2)	0.1545 (3)	0.0590 (5)	0.5590 (11)
C(3)	0.1558 (3)	–0.0300 (6)	0.5766 (10)
C(4)	0.0291 (2)	0.0905 (5)	1.0543 (9)
C(5)	0.0615 (2)	0.0609 (5)	1.1463 (10)
C(6)	0.0675 (2)	–0.0262 (5)	1.1415 (9)
C(7)	0.2362 (3)	0.0312 (8)	0.9894 (13)
C(8)	0.2238 (4)	0.0896 (9)	1.0837 (15)
C(9)	0.2001 (4)	0.0595 (9)	1.1923 (16)
C(10)	0.1598 (4)	0.25	0.8055 (14)
C(11)	0.1240 (4)	0.25	1.0406 (15)
C(12)[a]	0.1531 (5)	0.2200 (9)	0.9563 (21)

[a] Occupancy 0.5 (imposed by a mirror plane).

Table V. $[Et_4N]_2[Ni_6(pdt)_7]$: Selected Distances and Angles of the $[Ni_6(pdt)_7]^{2-}$ Anion[a]

	Distances (Å)		
Ni(1′)–Ni(1)	2.843 (2)	Ni(1)–S(1)	2.204 (2)
Ni(1)–Ni(2)	2.750 (2)	Ni(1)–S(2)	2.200 (2)
Ni(2)–Ni(3)	2.822 (2)	Ni(1)–S(3)	2.185 (3)
S(1)–S(2)	2.795 (4)	Ni(1)–S(4)	2.188 (2)
S(3)–S(4)	2.945 (4)	Ni(2)–S(1)	2.192 (2)
S(5)–S(6)	2.769 (4)	Ni(2)–S(2)	2.186 (2)
S(7)–S(8)	3.251 (4)	Ni(2)–S(5)	2.188 (2)
S(1)–S(4)	3.320 (4)	Ni(2)–S(6)	2.175 (2)
S(2)–S(3)	3.312 (4)	Ni(3)–S(5)	2.226 (3)
S(1)–S(5)	3.370 (4)	Ni(3)–S(6)	2.247 (3)
S(2)–S(6)	3.368 (4)	Ni(3)–S(7)	2.161 (3)
S(5)–S(7)	3.168 (4)	Ni(3)–S(8)	2.153 (3)
S(6)–S(8)	3.200 (4)		
	Angles (deg)		
Ni(1′)–Ni(1)–Ni(2)	177.3 (1)	S(1)–Ni(2)–S(2)	79.4 (1)
Ni(1)–Ni(2)–Ni(3)	105.6 (1)	S(5)–Ni(2)–S(6)	78.8 (1)
Ni(1)–S(1)–Ni(2)	77.5 (1)	S(1)–Ni(2)–S(5)	100.6 (1)
Ni(1)–S(2)–Ni(2)	77.7 (1)	S(2)–Ni(2)–S(6)	101.1 (1)
Ni(1)–S(3)–Ni(1′)	81.2 (1)	S(1)–Ni(2)–S(6)	177.6 (1)
Ni(1)–S(4)–Ni(1′)	81.1 (1)	S(2)–Ni(2)–S(5)	178.0 (1)
Ni(2)–S(5)–Ni(3)	79.5 (1)	S(5)–Ni(3)–S(6)	76.5 (1)
Ni(2)–S(6)–Ni(3)	79.3 (1)	S(7)–Ni(3)–S(8)	97.8 (1)
S(1)–Ni(1)–S(2)	78.8 (1)	S(5)–Ni(3)–S(7)	92.4 (1)
S(3)–Ni(1)–S(4)	84.7 (1)	S(6)–Ni(3)–S(8)	93.3 (1)
S(2)–Ni(1)–S(3)	98.1 (1)	S(5)–Ni(3)–S(8)	169.3 (1)
S(1)–Ni(1)–S(4)	98.2 (1)	S(6)–Ni(3)–S(7)	168.9 (1)
S(1)–Ni(1)–S(3)	175.7 (1)		
S(2)–Ni(1)–S(4)	175.4 (1)		

[a] The primed atoms are related to the unprimed ones by the symmetry transformation x, $0.5 - y$, z.

Table VI. $[Ph_4P]_2[Ni_3(edt)_4]$: Atomic Coordinates of the $[Ni_3(edt)_4]^{2-}$ Anion without H Atoms

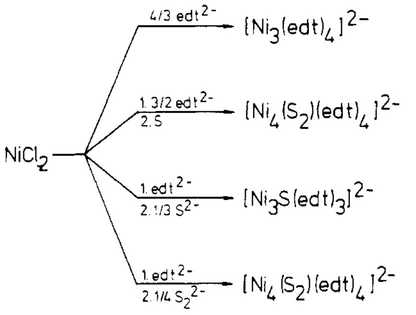
atom	*x*	*y*	*z*
Ni(1)	0.0	0.0	0.0
Ni(2)	0.10048 (4)	0.24860 (4)	0.17593 (3)
S(1)	−0.11895 (9)	0.06731 (8)	0.10905 (6)
S(2)	−0.00512 (9)	0.38616 (9)	0.18061 (7)
S(3)	0.18605 (9)	0.09548 (8)	0.14596 (6)
S(4)	0.33154 (9)	0.41870 (8)	0.23413 (7)
C(1)	−0.2408 (4)	0.1331 (3)	0.0525 (3)
C(2)	−0.2080 (3)	0.2698 (3)	0.1329 (3)
C(3)	0.3739 (4)	0.1949 (3)	0.1362 (3)
C(4)	0.4484 (4)	0.3271 (3)	0.2323 (3)

Table VII. $[Ph_4P]_2[Ni_3(edt)_4]$: Selected Distances and Angles of the $[Ni_3(edt)_4]^{2-}$ Anion[a]

	Distances (Å)		
Ni(1)–S(1)	2.210 (1) (2×)	Ni(1)–Ni(2)	2.856 (1)
Ni(1)–S(3)	2.189 (1) (2×)	S(1)–S(2)	2.881 (1)
Ni(2)–S(1)	2.174 (1)	S(1)–S(2′)	3.324 (1)
Ni(2)–S(2)	2.181 (1)	S(1)–S(3)	3.131 (1)
Ni(2)–S(3)	2.179 (1)	S(2)–S(4)	3.142 (1)
Ni(2)–S(4)	2.196 (1)	S(3)–S(4)	3.176 (1)
	Angles (deg)		
S(1)–Ni(1)–S(3)	81.8 (1) (2×)	S(1)–Ni(2)–S(2)	91.9 (1)
S(1)–Ni(1)–S(1′)	180.0	S(1)–Ni(2)–S(3)	82.9 (1)
S(1)–Ni(1)–S(3′)	98.2 (1) (2×)	S(1)–Ni(2)–S(4)	174.1 (1)
S(3)–Ni(1)–S(3′)	180.0	S(2)–Ni(2)–S(3)	171.2 (1)
Ni(1)–S(1)–Ni(2)	81.3 (1) (2×)	S(2)–Ni(2)–S(4)	93.0 (1)
Ni(1)–S(3)–Ni(2)	81.6 (1) (2×)	S(3)–Ni(2)–S(4)	91.8 (1)

[a] The primed atoms are related to the unprimed ones by the symmetry transformation $\bar{x}, \bar{y}, \bar{z}$.

Scheme I

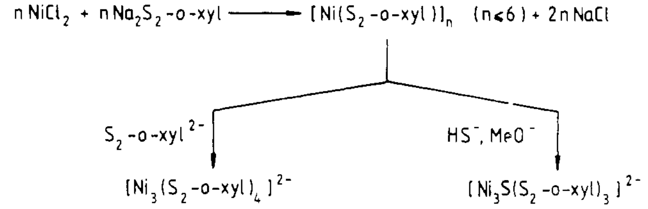


fields (1.26, 2.59, 3.78, and 5.06 kG) with the Gouy method.[39] Diamagnetic corrections[39] were applied. ^1H NMR spectra were recorded on a Bruker WM 300 spectrometer with TMS as internal standard.

Results

Synthesis. In our attempts to develop synthetic routes to new Ni–S–SR compounds we have explored the reaction systems Ni(II)/dithiolate/X (dithiolate = edt^{2-}, pdt^{2-}, S_2-*o*-xyl^{2-}; X = S^{2-}, S_2^{2-}, S, thiolate). This choice was based on the observation that depending on the dithiole employed in a given reaction system, e.g. $FeCl_3$/dithiolate/S^{2-}, very different products could be isolated.[19a,b,31] For dithiolate = edt^{2-}, S_2-*o*-xyl^{2-}, and $S(CH_2)_6S^{2-}$ or $S(CH_2)_2S(CH_2)_2S^{2-}$, $[Fe_2(edt)_4]^{2-}$,[19d,e] $[Fe_2S_2(S_2\text{-}o\text{-}xyl)_2]^{2-}$,[31b] and $[Fe_4S_4(SRS)_2]^{2-}$[31d] could be obtained. Likewise in the system $MnCl_2$/dithiolate, $[Mn(tdt)_2]^{2-}$ was isolated for dithiolate = tdt^{2-},[21] and $[Mn_2(S_2\text{-}o\text{-}xyl)_3]^{2-}$ was found if S_2-*o*-xyl^{2-} was used as the dithiolate component.[28a,b] Descriptions of the reactions, structures, and selected properties of the products are provided in the sequel. A summary of the reactions studied is given in Schemes I and II.

Scheme II



Initial studies of the solution equilibria relevant to the formation of Ni^{II}–thiolate complexes were made by Leussing, who reported the generation of hydroxypropane-2,3-dithiolate[40a] and edt^{2-}[40b] in aqueous alkaline solutions. We found that reaction of $NiCl_2$ with 1 equiv of various dithiolates in each case results in the formation of intractible brown solids with analytical composition Ni(dithiolate). Reaction of these solids with an excess of dithiolate produced brown solutions, from which the anions $[Ni_3(S_2\text{-}o\text{-}xyl)_4]^{2-}$ (**1**), $[Ni_3(edt)_4]^{2-}$ (**2**), and $[Ni_6(pdt)_7]^{2-}$ (**3**) could be precipitated with quaternary cations.[40c] The reaction system $NiCl_2/pdt^{2-}$ has been investigated in acetone and acetonitrile. For nickel/dithiolate ratios between 1:1.2 and 1:2 **3** is preferentially formed in both solvents as detected by electronic spectra. For smaller ratios we observed the incipient formation of the binuclear species $[Ni_2(pdt)_3]^{2-}$.[40d]

In the system $NiCl_2/S_2\text{-}o\text{-}xyl^{2-}/X$ (X = S_2-*o*-xyl^{2-}) the anion **1** is formed with an excess of S_2-*o*-xyl^{2-}. A $[Ni_2(S_2\text{-}o\text{-}xyl)_3]^{2-}$ species, whose visible spectrum is different from that of $[Ni_3(S_2\text{-}o\text{-}xyl)_4]^{2-}$, has been reported earlier by Lane et al.,[31b] but no structural information was given. We have not been able to isolate a material with this composition from methanol solutions. Upon reaction of the initial precipitate with Li_2S in methanol the trinuclear complex $[Ni_3S(S_2\text{-}o\text{-}xyl)_3]^{2-}$ (**8**) is formed.[29c]

Treating the initial precipitate with monofunctional ligands such as SPh^- affords brown solutions of soluble thiolate species; products other than **1** have not been characterized yet. Replacement of SPh^- by 1,1-dithio ligands such as dithiocarbamate gave only intractible brown solids and essentially colorless supernatants.

From the reaction system $NiCl_2/edt^{2-}/X$ (X = edt^{2-}, S, S_2^{2-}, S^{2-}) the new homoleptic thiolate complex **2** was obtained in excess of edt^{2-} in methanol. For nickel–dithiolate ratios smaller than 1:3.5, **2** was the only product isolated rather than $[Ni(edt)_2]^{2-}$, $[Ni_2(edt)_3]^{2-}$, or higher condensed species. Larger excesses of dithiolate have not been used in this work. Snyder et al.[5c] reported the formation of $[Ni_2(edt)_3]^{2-}$ from $NiCl_2\cdot 6H_2O$ and H_2edt in methanolic solution, where KOH was used to generate edt^{2-} from the dithiole. The synthesis of Et_4N^+ salts of $[Ni_2(edt)_3]^{2-}$ and **2** from $[Et_4N]_2[NiBr_4]$ and Na_2edt in acetonitrile including some spectral and electrochemical data has been reported by Yamamura et al.[3d] Reaction of the initial precipitate with sulfur or disulfide in ratios of 2:1 (and less) resulted in the formation of the $[Ni_4(S_2)(edt)_4]^{2-}$ anion (**7**), which could be isolated as Ph_4P^+ salt in high yields. Adding S^{2-} afforded a material with composition $[Ni_3(S(edt)_3]^{2-}$. Interestingly, a $[Ni_3S(SMe)_6]^{2-}$ complex (**9**) could

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(39) Weiss, A.; Witte, H. *Magnetochemie*; Verlag Chemie: Weinheim, West Germany, 1973.

(40) (a) Leussing, D. L. *J. Am. Chem. Soc.* **1959**, *81*, 4208. (b) Leussing, D. L.; Alberts, G. S. *J. Am. Chem. Soc.* **1960**, *82*, 4458. (c) Another independent report (ref 3d) of the Ni(II)/edt^{2-} system appeared while this work was in progress. Subsequent to our preliminary report (ref 32), an investigation of this reaction system in EtOH was published: Nicholson, J. R.; Christou, G.; Huffman, J. C.; Folting, K. *Polyhedron* **1987**, *6*, 863. Surprisingly, **5** was found to crystallize in the monoclinic space group $P2_1/n$ (instead of $P\bar{1}$). The molecular weight and density of **5** are incorrectly given in this paper. (d) $[Et_4N]_2[Ni_2(pdt)_3]\cdot CH_3CN$ crystallizes in the orthorhombic space group $Pna2_1$ with a = 16.204 (5) Å, b = 19.530 (7) Å, c = 11.274 (4) Å, and Z = 4. Suitable single crystals were difficult to obtain and high-quality X-ray diffraction data could not be collected. For this reason the crystal structure, which, however, could be solved, is not reported in detail here. The general appearance of the $[Ni_2(pdt)_3]^{2-}$ anion resembles that of the $[Ni_2(edt)_3]^{2-}$ anion from ref 5c and 40c. The central NiS_4 fragments are essentially planar, but the entire Ni_2S_6 framework is bent, the dihedral angle being 116.8°. The mean Ni–S distances and Ni–S_b–Ni and S_b–Ni–S_b angles are 2.200 Å, 83.3°, and 79.6°, respectively. The Ni···Ni distance is 2.941 (4) Å.

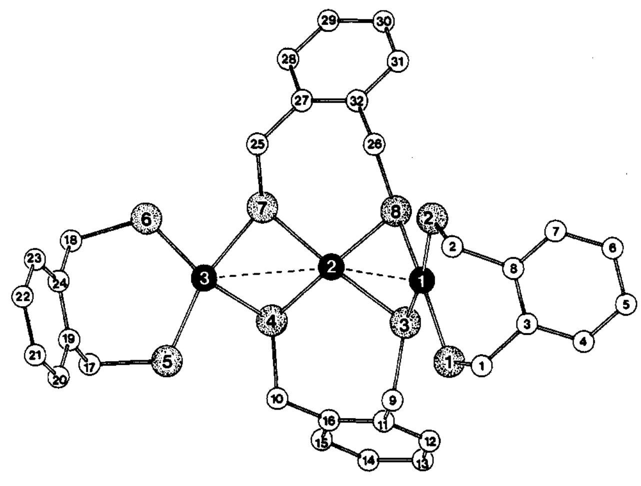


Figure 1. Structure of the [Ni$_3$(S$_2$-*o*-xyl)$_4$]$^{2-}$ anion (1) with atomic labeling scheme.

be obtained from NiCl$_2$ and NaSMe (1:4.4) in acetonitrile.[41] Reaction with monofunctional thiolates yields soluble products different from **2** and [Ni$_2$(edt)$_3$]$^{2-}$ currently under investigation.

Description of the Structures. The crystal structures of the three homoleptic thiolate salts (see Table I) consist of well-separated cations and anions. In the case of **4**, methanol molecules are also present. The structures of the cations are unexceptional and will not be discussed here. For the purpose of clarity, the atoms in the two-dimensional representations of the anions are shown as spheres of arbitrary radius (Ni, black; S, dotted; C, white).

[Ni$_3$(S$_2$-*o*-xyl)$_4$]$^{2-}$. The structure of **1** with the atomic labeling scheme (different from that originally given in ref 5b) is depicted in Figure 1.

The complex may be viewed as a [Ni(S$_2$-*o*-xyl)$_2$]$^{2-}$ unit, to which two Ni(S$_2$-*o*-xyl) fragments are cis bonded. As a result, the sulfur atoms S(3), S(4), S(7), and S(8) are each in bridging positions. The Ni$_3$S$_8$ core of **1** is built up from three edge-linked square-planar NiS$_4$ units (dihedral angles; 123.4 and 131.6°) connected in a cis fashion with respect to the central Ni site. From this point of view the Ni$_3$S$_8$ framework resembles the corresponding moiety in cyclic complexes such as [Ni$_6$(SEt)$_{12}$][4c] or [Ni$_8$-(SCH$_2$CH$_i$COOEt)$_{16}$].[4e] The three nickel atoms are arranged at an angle of 131.34° (120.0° in [Ni$_6$(SEt)$_{12}$] and 135° in [Ni$_8$(SCH$_2$CH$_2$COOEt)$_{16}$]) with each four of the eight sulfur atoms lying between 1.35 and 1.75 Å above and below the plane containing the metal atoms. The three NiS$_4$ units are only slightly nonplanar as judged by their mean planes. Atom Ni(2) is 0.107 Å out of the mean plane defined by the atoms S(3), S(4), S(7), and S(8). The principal geometrical features of the Ni$_3$S$_8$ core are as follows: (i) The average Ni–S$_t$ and Ni–S$_b$ distances are 2.185 and 2.213 Å, respectively; similar distances are found in other nickel thiolate compounds.[5a–c,41–44] The bridging Ni–S$_b$ distances are slightly longer than the terminal ones. (ii) The Ni–Ni distances are 3.131 (1) and 3.016 (1) Å and thus outside the range for direct metal–metal interactions. (iii) The S–Ni–S angles can be organized in three groups: angles within the seven-membered chelate rings, angles within the cyclic Ni$_2$S$_2$ moieties, and angles of the type S$_t$–Ni–S$_b$, the average values for each group being 103.7, 75.6, and 90.6° (another group not mentioned here contains the angles near 180°). The Ni–S$_b$–Ni angles average to 88.0°, which is a considerably larger value than in related compounds,[4,5a,c,41–44] [Ni$_3$(SEt)$_8$]$^{2-}$ [5a] being the only complex where a comparable Ni–S$_b$–Ni angle of 87° has been reported. Striking features of **1** are the very short interchelate S–S distances of 2.735

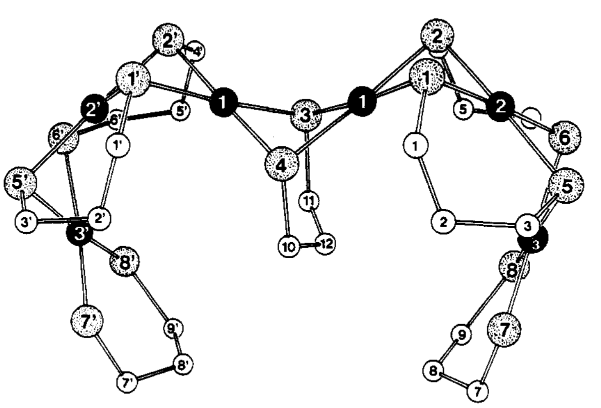
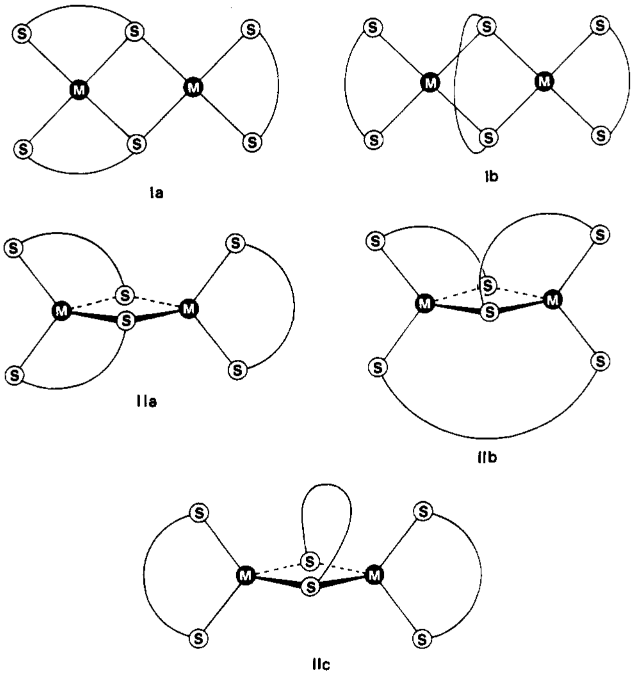


Figure 2. Structure of the [Ni$_6$(pdt)$_7$]$^{2-}$ anion (3) with atomic labeling scheme.



Ia

Ib

IIa

IIb

IIc

Figure 3. Possible structures of dinuclear tetracoordinated metal(II) dithiolates [M$_2$(SRS)$_3$]$^{2-}$: Ia,b square planar; IIa–c tetrahedral metal coordination.

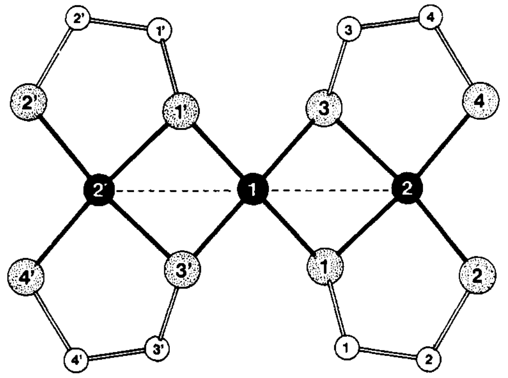


Figure 4. Structure of the [Ni$_3$(edt)$_4$)]$^{2-}$ anion (2) with atomic labeling scheme.

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(41) Matsumoto, K.; Kriege, M.; Henkel, G. *J. Chem. Soc., Dalton Trans.* **1988**, 657.

(42) Barclay, G. A.; McPartlin, E. M.; Stephenson, N. C. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 1262.

(43) A number of trinuclear Ni^{II} species with S and N ligands have been characterized structurally: (a) Wei, C. H.; Dahl, L. F. *Inorg. Chem.* **1970**, *9*, 1878. (b) Drew, M. G. B.; Rice, D. A.; Richards, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 2075. (c) Weiss, J. *Angew. Chem.* **1984**, *96*, 232; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 225. (d) A complex [Ni$_3$L$_2$]Cl$_2$·4H$_2$O (LH$_2$ = *N,N'*-dimethylbis(2-mercaptoethyl)ethylenediamine) was prepared and structurally characterized in 1975: Trimakis, A.; Rabinowitz, H. N.; Lippard, S. J., unpublished results (cited in ref 44a).

(44) (a) Gibson, D.; Lippard, S. J. *Inorg. Chem.* **1986**, *25*, 219. (b) Suades, J.; Solans, X.; Font-Altaba, M. *Polyhedron* **1984**, *3*, 1227. (c) Barrera, H.; Bayon, J. C.; Suades, J.; German, C.; Declerq, J. P. *Polyhedron* **1984**, *3*, 969.

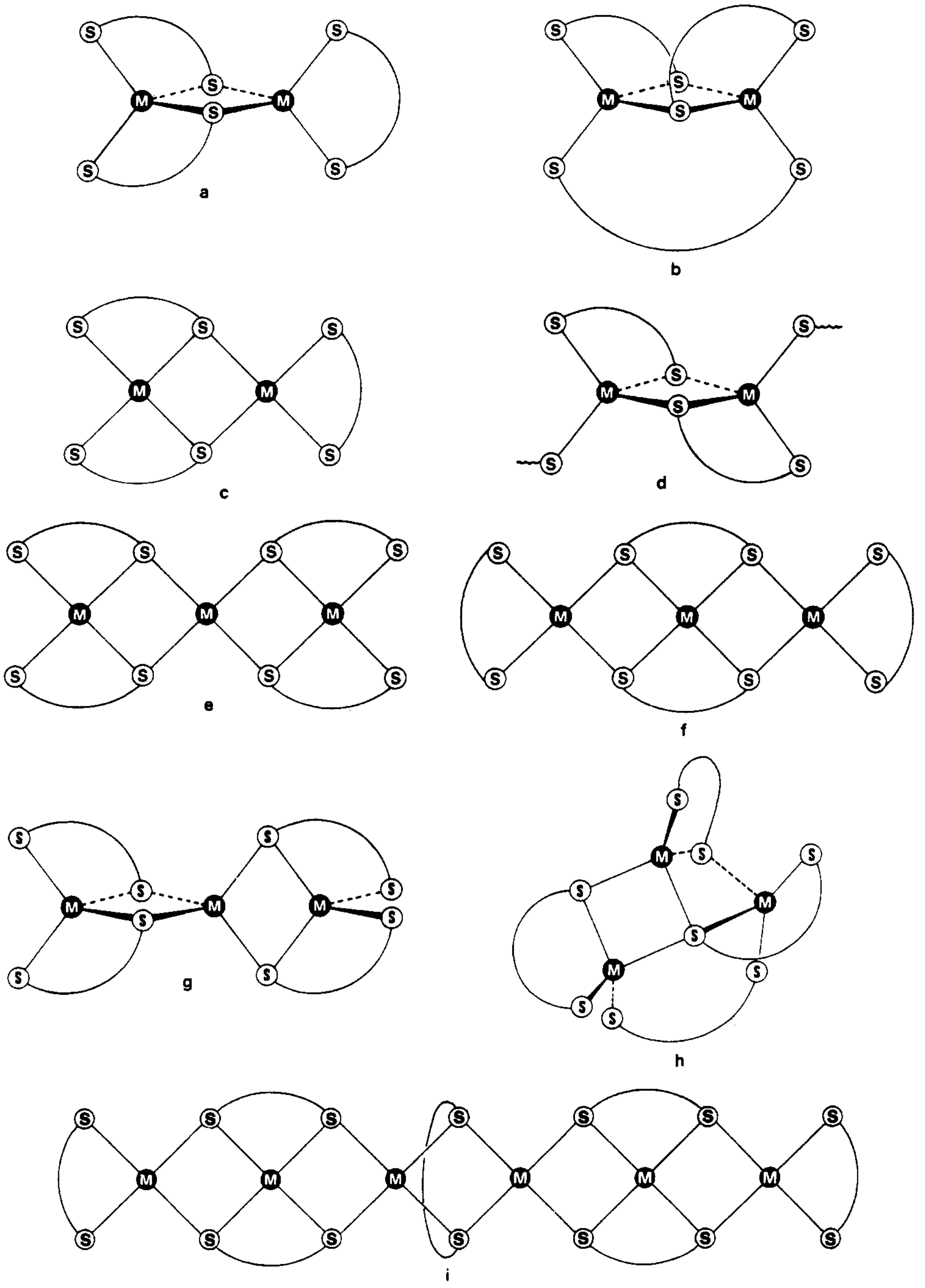

Figure 5. Structures of tetracoordinated metal(II) dithiolates that have been crystallographically established: (a) $[M_2(S_2\text{-}o\text{-xyl})_3]^{2-}$ (M = Fe, Zn) (ref 28); (b) $[M_2(S_2\text{-}o\text{-xyl})_3]^{2-}$ (M = Mn, Fe, Co, Cd) (ref 27a, 28a); (c) $[Ni_2(edt)_3]^{2-}$ (ref 5c, 40c); (d) $[Hg_2(edt)_3]^{2-}$ (ref 22); (e) $[Ni_3(edt)_4]^{2-}$ (ref 32, 40c; this work); (f) $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ (ref 28a; this work); (g) $[Hg_3(edt)_4]^{2-}$ (ref 22); (h) $[Hg_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ (ref 30b); (i) $[Ni_6(pdt)_7]^{2-}$ (this work). Mononuclear species are not shown.

(S(4)–S(7)) and 2.687 Å (S(3)–S(8)) between the bridging sulfur atoms. These distances are ca. 1 Å shorter than the van der Waals nonbonding distances and 0.2 Å shorter than the corresponding distances in other sulfur-bridged nickel compounds.[5c,41–44]

$[Ni_6(pdt)_7]^{2-}$. The structure of **3** with atomic labeling scheme is displayed in Figure 2. The core structure of the hexanuclear $[Ni_6(pdt)_7]^{2-}$ anion is built up from approximately square-planar NiS_4 coordination units which share common edges.

The molecular structure can be derived from a hypothetical $[Ni(pdt)_2]^{2-}$ anion, to which a Ni(pdt) fragment is linked in a cis fashion resulting in a $[Ni_2(pdt)_3]^{2-}$ subunit. Two of these subunits are connected by a central $[Ni(pdt)Ni]^{2+}$ moiety to yield the hexanuclear anion **3**. From another point of view this anion may be considered to be built up from two $[Ni_3(pdt)_4]^{2-}$ subunits that share a common pdt^{2-} ligand. Each trinuclear subunit has a conformation similar to that of $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$. The complex is situated on a crystallographic mirror plane and approaches C_{2v} symmetry. A conspicuous feature of **3** is the central bridging ligand.

Binuclear complexes containing 1,*n*-dithiolate ligands ($n > 4$) may occur in two (square-planar coordination) or three (tetrahedral coordination) isomeric forms as displayed in Figure 3 schematically.

Structure types Ia,[5c] IIa,[28] and IIb[28a] have been established for metal(II) dithiolate complexes; type Ib and IIc with syn bridging ligands have not been reported so far. Complex **3** described here represents the first example containing a bridging ligand of type Ib in compounds with square-planar metal coordination. Given $S_b \cdots S_b$ distances of approximately 3.637 Å in tetrahedrally coordinated compounds, the experimentally unrealized structure IIc would presumably be unfavorable due to steric interactions.

Different from the cyclic hexanuclear complex $[Ni_6(SEt)_{12}]$,[4c] where the six NiS_4 units that build up the Ni–S framework are arranged in an all-cis fashion, the present case exhibits a cis–

trans–cis orientation. From the valence angles within the Ni_2S_2 rhombs and the calculated best planes of individual NiS_4 units, slight deviations from planarity are apparent, the nickel atoms Ni(1), Ni(2), and Ni(3) being 0.025, 0.040, and 0.065 Å out of the mean planes defined by the sulfur atoms surrounding them. Chemically equivalent bonds and angles involving only nickel and sulfur atoms occur in pairs of almost identical dimensions. The Ni–S bonds of the anion are of (at least) three different types according to their lengths. (i) The terminal Ni(3)–S_t bonds average 2.157 Å, which agrees well with the corresponding values in $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ and other related compounds.[5c,41–44] The bridging Ni(3)–S_b distances (average 2.237 Å) are significantly longer than those of the Ni(2)–S_b bonds within the six-membered chelate rings (average 2.185 Å). The Ni(1)–S(1,2) distances average 2.202 Å, in an intermediate range, whereas the Ni(1)–S(3,4) distances (average 2.186 Å) are similar to those formed by Ni(2). As in all other known polynuclear nickel thiolate complexes except $[Ni_2(SEt)_6]^{2-}$,[5a] the Ni_2S_2 moieties are folded along their S···S vectors, the fold angles between the S_4 planes ranging between 109.5° and 119.8°. The terminal $[Ni_2(pdt)_3]^{2-}$ fragments exhibit a remarkable similarity to the $[Ni_2(edt)_3]^{2-}$ anion reported recently[5c] if their Ni–S frames are compared. With emphasis on this relationship, $[Ni_6(pdt)_7]^{2-}$ can be assembled from two binuclear subunits in a conformation similar to those observed in $[Ni_2(edt)_3]^{2-}$, where the subunits are linked by a central $[Ni_2(pdt)]^{2+}$ entity. The S_b–Ni–S_b angles within the central Ni_2S_2 portion are 84.7°; the S_b–Ni–S_b angles within the two outer Ni_2S_2 units average to 78.4° with individual values between 76.5 (1) and 79.4 (1)°. The Ni–S_b–Ni angles occur in pairs with average values of 81.2 (S(3,4)), 77.6 (S(1,2)), and 79.4° (S(5,6)). The differences in these angles are reflected in the corresponding Ni–Ni separations of 2.843 (2) (Ni(1)–Ni(1′)), 2.750 (2) (Ni(1)–Ni(2)), and 2.822 (2) Å (Ni(2)–Ni(3)). The S_t–Ni(3)–S_t and the S_b–Ni(2)–S_b angles within the chelating units are 97.8 and 100.9° (S(1)–Ni(2)–S(5), S(2)–Ni(2)–S(6)) on average; these values are considerably larger than the S_b–Ni–S_b angle found within the Ni_2S_2 moieties. As in $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$, the shortest S···S contacts are between the sulfur atoms within the Ni_2S_2 rhombs, the individual values being 2.795 (4) (S(1,2)), 2.769 (4) (S(5,6)), and 2.945 (4) Å (S(3,4)) to be contrasted with 3.251 Å between S(7,8) within the terminal chelate ring. The former values are approximately 0.1–0.2 Å longer than the corresponding distances in $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$.

$[Ni_3(edt)_4]^{2-}$. The structure of 2 with the atomic labeling scheme is depicted in Figure 4. The $[Ni_3(edt)_4]^{2-}$ anions occupy crystallographic inversion centers.

As a result, the metal part of the complex is strictly linear. The central nickel atom is chelated by two identical $Ni(edt)_2$ fragments. The average Ni–S distance within these fragments is 2.183 Å compared to 2.200 Å around Ni(1). The planarity of the central NiS_4 unit is required by symmetry; only small distortions from planarity are observed for the outer NiS_4 entities. The three NiS_4 units are condensed via opposite edges in a trans (chair) fashion to form the Ni_3S_8 core of the anion. It is interesting to note that the condensation is cis (boat) in $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ and mixed cis–trans in $[Ni_6(pdt)_7]^{2-}$. As in the other two cases, there are folds along the S···S vectors of the Ni_2S_2 units, the dihedral angle being 116.8°. The Ni–Ni separation is 2.856 (1) Å; the corresponding Ni–S_b–Ni angles average to 81.5°.

The nonbonded distance between S(1) and S(3) (2.881 (1) Å) is significantly longer than the corresponding values in $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ and $[Ni_6(pdt)_7]^{2-}$.

Discussion

The structures of the complexes described together with the structures of other four-coordinate complexes containing chelating ligands[5c,42–44] raise some interesting speculations concerning their formation. Structure types (of discrete metal(II) thiolates with chelating ligands) that have been crystallographically characterized are displayed in Figure 5 schematically.

As suggested by Snyder et al.,[5c] $[Ni_2(edt)_3]^{2-}$ is generated in solution by reaction of a solvated Ni(edt) species with $[Ni(edt)_2]^{2-}$, and the solid-state structure of $[Ni_2(edt)_3]^{2-}$ can be rationalized by using that mechanism. In a similar manner the anion $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ can be considered as an extension of a binuclear $[Ni_2(dithiolate)_3]^{2-}$ precursor with one Ni(dithiolate) fragment attached on the opposite side. The proposed reaction mechanism[5c] and the associated construction principle fail for $[Ni_3(edt)_4]^{2-}$, the structure of which can easily be decomposed in terms of two $[Ni(edt)_2]^{2-}$ anions and a central Ni^{2+} (neglecting for the time being how this may be generated in solution). Similarly, the existence of related species such as $[Hg_3(edt)_4]^{2-}$[22] (although having metal atoms in tetrahedral coordination) solidifies the above description for $[Ni_3(edt)_4]^{2-}$. If the same manner of fragmentation is used, the structure of $[Ni_6(pdt)_7]^{2-}$ could be rationalized in terms of one $[Ni_3(pdt)_4]^{2-}$ anion, one $[Ni_2(pdt)_3]^{2-}$ anion, and one additional Ni^{2+} cation linking both units. Of course, other ways of formation of metal dithiolate complexes are possible, e.g. linkage of building blocks to form quasi-polymeric species, as in $[Hg_2(edt)_3]^{2-}$.[22]

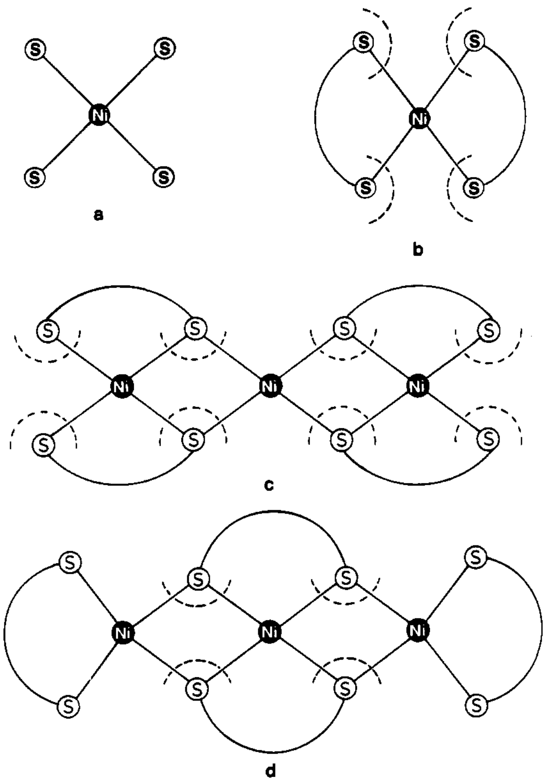

Figure 6. Schematic illustration of the different $[Ni_3(SRS)_4]^{2-}$ isomers depending on the ligand SRS^{2-}: (a) Undistorted $[Ni(SR)_4]^{2-}$, no ligand strain imposed; (b) $[Ni(SRS)_2]^{2-}$ with chelating SRS^{2-} ligands, with both ligand strain and S···S repulsion determining the distortion around the Ni atom; (c,d) trinuclear $[Ni_3(SRS)_4]^{2-}$. Structure d is favored compared to structure c for the case of ligands with large bite distances due to additional S···S repulsion.

Formation of the $[Ni_3(edt)_4]^{2-}$ and $[Ni_6(pdt)_7]^{2-}$ anions probably proceeds through complicated multistep mechanisms.[45] Although we have not studied the mechanisms of the reactions described in this paper, it seems intuitively appealing to postulate a solvent promoted substitution of a bridging thiolate ligand in polymeric Ni(thiolate) as the initial reaction step. In the subsequent displacement steps, different bridging dithiolate ligands are competing for metal coordination sites. The mechanism of the condensation steps to form the trinuclear, hexanuclear, and other still unidentified products is obscure, and the nature of the solvent may be significant.[45]

Comparative Structural Features. The anions $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$, $[Ni_3(edt)_4]^{2-}$,[5c,40c] and $[Ni_6(pdt)_7]^{2-}$, together with $[Ni_3(SCH_2CH_2NH_2)_4]^{2+}$,[43a] $[Ni_3(S_2N_2)_4]^{2-}$,[43c] and $[Ni_3(SEt)_8]^{2-}$[5a]

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(45) For a general review of substitution reactions of square-planar complexes involving polydentate ligands see: Mureinik, R. J. *Rev. Inorg. Chem.* **1979**, *1*, 11.

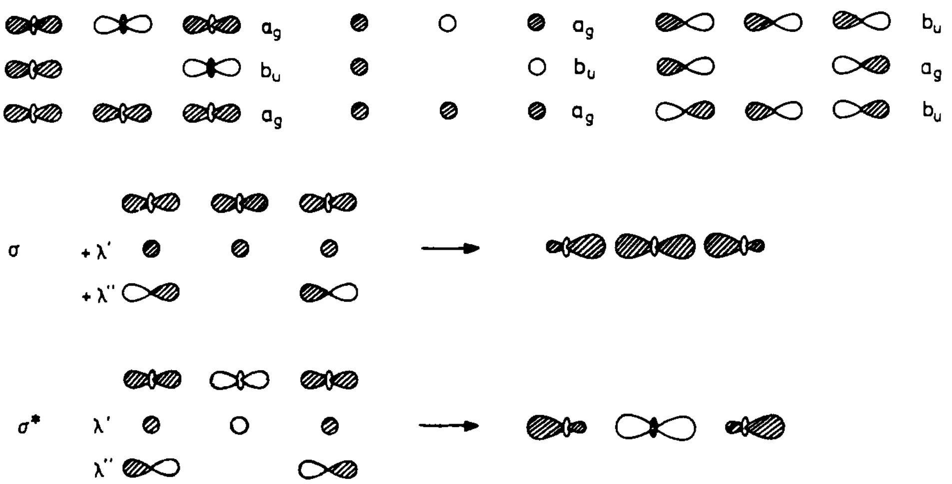

Figure 7. Illustration of possible attractive interactions between the Ni(II) atoms in $[Ni_3(SRS)_4]^{2-}$ complexes. Top row: linear combination of 3d, 4s, and 4p orbitals of the Ni atoms gives bonding, nonbonding and antibonding combinations. Middle and bottom row: mixing of the orbitals of proper symmetry stabilizes the 3d orbital set. The σ combination (middle row) becomes more bonding, and the σ* combination becomes less antibonding (bottom row) moving partway to a lone-pair combination.

reported earlier, constitute a set of nickel thiolate complexes with proven structure. All compounds exhibit the intrinsic geometrical preference of the Ni(II) ions with structural constraints of the ligands superimposed. Earlier investigations[5a,c,42–44] and the present study have established the structures of some acyclic trinuclear complexes. One of these, $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$, exists in structure type I (Figure 6d), whereas the other three occur as type II compounds (Figure 6c). It is worthwhile mentioning that all type II trimers have 1,2-bifunctional ligands attached, whereas a 1,4-dithiolate ligand is coordinated in the type I compound. Two factors may be responsible for this structural preference: (i) the range of possible bite distances of the chelating ligand or (ii) steric interactions between the ligands. From structural models it can be shown that steric interactions between the ligands are only of minor importance; so one is left with the ligand bite distance as the crucial point.

When the geometry of the above complexes is reexamined, the following structural features are evident. (i) The nickel atoms reside in square-planar coordination. The deviations from the ideal geometry are revealed by the S–Ni–S angles or equivalently by the S⋯S distances around each nickel center. (ii) Given a square-planar coordination of nickel and Ni–S distances of approximately 2.20 Å, the sulfur atoms are to be found in the absence of ligand strain on a circle with radius 2.20 Å centered at nickel, their equilibrium positions being at the corners of a square with a side length of 3.11 Å (see Figure 6a). If one considers steric interactions of the ligands in the next step, the equilibrium positions of the sulfur atoms are determined by ligand strain and S⋯S repulsion (see Figure 6b). For the $S_2\text{-}o\text{-xyl}^{2-}$ ligands, there is considerable steric strain as evidenced by the average bite angles of 103.9° within the terminal Ni(dithiolate) groups in **1**, the corresponding value in $[Ni_2(edt)_3]^{2-}$ being 92.2°. The associated intraligand S⋯S distances in these two complexes are 3.440 and 3.123 Å, respectively. As a consequence, the average S_b–Ni–S_b angle within the Ni_2S_2 units in $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ is reduced to 75.6° as compared to 82.4° in $[Ni_3(edt)_4]^{2-}$. The corresponding interligand S⋯S distances within the Ni_2S_2 moieties of **1** and **2** are 2.711 and 2.881 Å, respectively. As shown schematically in Figure 6c, the coupling of two distorted $[Ni(S_2\text{-}o\text{-xyl})_2]^{2-}$ building blocks via a central nickel atom in the type II structure introduces two additional strong S⋯S repulsions. Therefore, the steric requirements of the large-bite ligand are accommodated much more easily in structure type I (Figure 6d). We do not see any steric interactions to prevent the $[Ni_3(edt)_4]^{2-}$ anion from adopting this structure type. In fact, isomers of other metal(II) thiolates with chelating ligands have been observed in several cases.[27a,28]

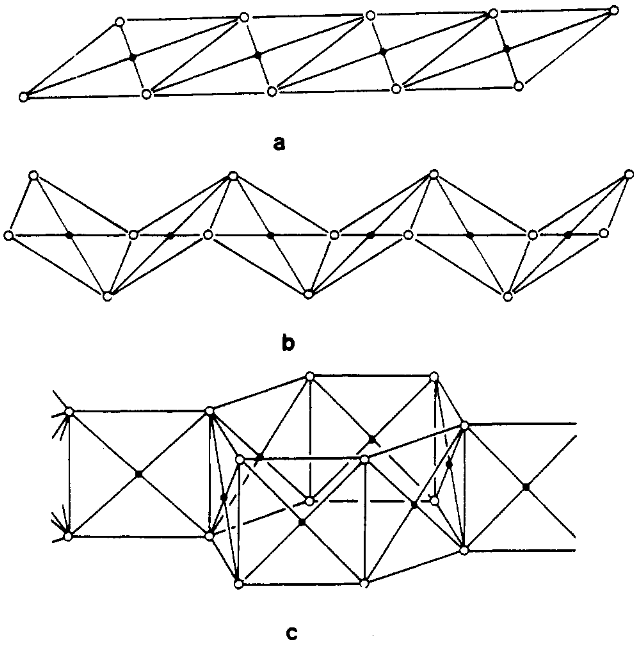

Figure 8. Three stereochemically distinct patterns containing square-planar NiS_4 subunits in extended lattices: (a) planar one-dimensional chain; (b) puckered one-dimensional chain; (c) honeycomb pattern.

Although it was concluded here that the dinuclear and trinuclear complexes adopt their principal molecular geometries essentially as a consequence of the chelating ligands, the cause of the nonplanar structure in the unconstrained $[Ni_3(SEt)_8]^{2-}$[5a] might be traced back to a tendency of sulfur to minimize the Ni–S–Ni valence angle, which is compensated by Ni⋯Ni repulsions. On the other hand, the Ni⋯Ni distances of 2.7–2.8 Å imply the possibility of weak Ni–Ni bonding interactions as can be rationalized by some qualitative MO arguments. Each Ni atom with a d^8 configuration has a filled $3d_{z^2}$ and empty 4s and 4p orbitals, which are available for metal–metal interaction. In the absence of s and p functions the closed-shell repulsion between the square-planar d^8 centers is evident. Mixing of metal s and p orbitals can convert this repulsion into a slight attraction. The mechanism by which 4s and 4p orbitals stabilize the trimer (and a dimer as well) is well understood.[46] From each of the 4s and $4p_z$ functions, one bonding, one nonbonding, and one antibonding combination of orbitals (a_g, b_u, a_g and b_u, a_g, b_u symmetry, respectively, assuming for example C_{2h} site symmetry of the Ni_3S_8 fragment) result. These mix into the occupied 3d combinations of proper symmetry in such a way as to stabilize the 3d σ and σ* orbitals. The σ orbital becomes more bonding and σ* less antibonding, moving partway to a lone-pair combination. The

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[46] See for example: Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187.

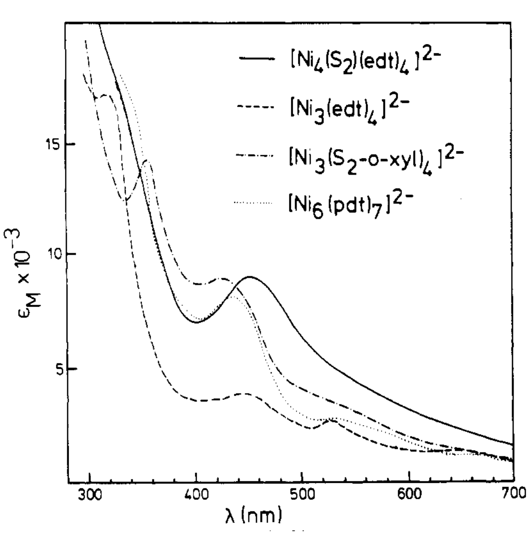

Figure 9. Electronic spectra of $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ (**1**), $[Ni_6(pdt)_7]^{2-}$ (**3**), $[Ni_3(edt)_4]^{2-}$ (**2**), and $[Ni_4(S_2)(edt)_4]^{2-}$ (**7**) in DMF solution (acetonitrile for **3**) at 25 °C.

mixing is illustrated schematically in Figure 7.

In practice, it may be difficult to distinguish the effects of direct Ni–Ni interactions and the stereochemical requirements of the ligands or bridging sulfur atoms. The centrosymmetric $[Ni_2(SEt)_6]^{2-}$ anion,[5a] with a reported Ni–Ni distance of 3.350 Å, and $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ so far are the only complexes where direct metal–metal interactions can be safely excluded. The arguments supplied here support a soft attractive Ni–Ni interaction overlaid on top of the ligand set requirements.

Related Solid-State Systems. All nickel thiolate compounds known (except for the tetrahedrally coordinated anions $[Ni(SPh)_4]^{2-}$[3a,b] and $[Ni(SC_6H_4Cl)_4]^{2-}$[3c]) contain square-planar NiS_4 subunits, from which possible Ni–S frameworks can be constructed. From a one-dimensional chain of edge-sharing NiS_4 units several stereochemically distinct patterns can be generated. Three of them are shown in Figure 8.

Patterns a (Figure 8a) and c (Figure 8c) have been observed in the solid-state compounds K_2PtS_4[14] and $A_2M_3S_4$ (A = Rb, Cs; M = Pd, Pt),[15] respectively, with metal–metal distances in the range between 3.1 and 3.2 Å. Fragments of the planar one-dimensional chain a are encountered in the anions $[Ni_2(SEt)_6]^{2-}$[5a] and $[Pd_2(SMe)_6]^{2-}$.[5f] The trinuclear anions $[Ni_3(edt)_4]^{2-}$, $[Ni_3(S_2N_2)_4]^{2-}$,[43c] and $[Ni_3(SEt)_8]^{2-}$[5a] (as well as the $[Ni_3(aet)_4]^{2+}$ cation[43a]) are fragments of the all-trans chain b. Fragments of the all-cis structure as found in the $A_2M_3S_4$ systems are the hexanuclear species $[Ni_6(SR)_{12}]$[4c,d] and $[Pd_6(SR)_{12}]$,[9] with $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ representing in turn a fragment of the hexameric molecule. The subunits of the hexanuclear $[Ni_6(pdt)_7]^{2-}$ anion can be viewed as a fragment of the $A_2M_3S_4$[15] structure as well. It is interesting to note that the pentanuclear complex $[Ni_5(SR)_{10}]$[4b] cannot find a counterpart due to the restrictions imposed by the translational symmetry of the crystal lattice.

Electronic Spectra and Magnetic Properties. Electronic spectra of **1**–**3** and **7** are provided in Figure 9 (DMF solutions except for **3** in which case acetonitrile was used). All spectra are dominated by strong charge-transfer bands between 350 and 500 nm trailing out into regions of higher wavelengths. These charge-transfer bands obscure possible ligand field transitions. No band assignment was attempted for this reason. The spectra are given for identification purposes.

1 exhibits two strong bands at (λ_{max}, nm (ϵ_M)) 356 (15 000) and 423 (8000). In the course of the syntheses of **2** the methanolic reaction solution is green, while solutions of 5 in DMF or acetonitrile are red-brown. DMF solutions of **5** show three bands at 316 (16900), 443 (3900), and 526 (2600) and one weak feature at 662 (1200) in reasonable agreement with ref 40c but different from that observed in ref 3d. The spectrum of the hexanuclear species **3** is quite similar with two absorptions at 435 (8600) and 530 (2900) and one weak feature at 667 (1200). Finally, the absorption spectrum of **7** is characterized by one single band at 453 (9000) and a poorly resolved shoulder at 354 nm.

For all materials the solid magnetic susceptibilities have been determined. Compounds **1**–**3** and **7** are all diamagnetic at room temperature, which is in accordance with square-planar coordinated Ni(II). Diamagnetic properties in solutions are indicated by sharp ^1H NMR resonances that are not shifted by more then ca. 0.5 ppm with respect to the free ligand signals.

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Registry No. **4**, 91281-86-6; **5**, 106317-25-3; **6**, 116663-39-9; **7**-$(Ph_4P)_2$, 106828-47-1.

Supplementary Material Available: Thermal parameters of the anions (Tables S-I–S-III), positional and thermal parameters of the cations and solvate molecules (Tables S-IV–S-VI), complete distances and angles within the anions, cations, and solvate molecules (Tables S-VII–S-IX), and stereoscopic views of anions **1**–**3** with thermal ellipsoids (Figures S-1–S-3) (18 pages); observed and calculated structure factors (Tables S-X–S-XII) (83 pages). Ordering information is given on any current masthead page.