Binuclear Nickel(II) and Copper(II) Complexes containing an Endogenous Alkanethiolato-bridging Sulphur Atom and Exogenous μ-Pyrazolate (pz) Group. Crystal Structure of $[Ni_2L(pz)]$ [L = *NN'*-3-mercaptopentane-1,5-diylbis(salicylideneiminate)(3−)]†

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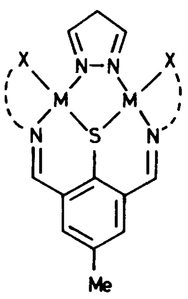
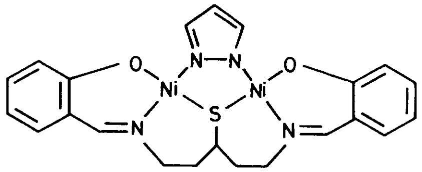
The first examples of binuclear nickel(II) and copper(II) complexes bonded to binucleating Schiff-base ligands containing an endogenous alkanethiolato-bridging sulphur atom have been synthesized. The complexes have the formula $[M_2L(pz)]$ (pz = pyrazolate) where L is the trianion of the pentadentate ligand *NN'*-3-mercaptopentane-1,5-diylbis(salicylideneimine). The pseudo-planar co-ordination spheres around M = Ni^{II} and Cu^{II} are completed by the *N*-donor atoms of an exogenous bridging μ-pyrazolate group. Crystals of $[Ni_2L(pz)]$ are monoclinic, space group $P2_1/c$ with $a = 9.679(4)$, $b = 8.860(4)$, $c = 24.711(9)$ Å, $\beta = 98.51(1)°$, $T = 20$ °C, $Z = 4$. The structure was solved by direct methods to $R = 0.065$ [$I \geqslant 3\sigma(I)$]. Both the NiN_2OS chromophores are distorted from planarity and are not coplanar. The Ni $\cdots$ Ni distance is 3.507(3) Å and Ni–S distances are 2.165(4) and 2.182(3) Å. A Ni–S–Ni bonding angle of 107.5(1)° was observed and the S atom adopts a pyramidal bridging arrangement. The copper(II) complex represents one of the few known stable alkanethiolate species. Variable-temperature magnetic susceptibility measurements show a small decrease of μ_{Cu} with decreasing temperature indicative of weak antiferromagnetic exchange coupling. The analogous alcoholato *O*-bridged complex is much more strongly coupled due, primarily, to the (presumed) trigonal-planar geometry at the bridging oxygen atom.

There is much current interest in binucleating ligands and their transition-metal complexes with emphasis being placed on structure/magnetism correlations and on bioinorganic modelling studies, *e.g.* for Cu^{II}–Cu^{II} Type 3 sites.[1–3] The great majority of these studies have involved the use of O atom endogenous bridging groups such as phenolate or alcoholate. Only recently have *S*-bridging thiophenolate groups in such binucleating ligands been synthesized by Krautil and Robson.[4] Structural and magnetic data on Pd^{II}–Pd^{II} and Cu^{II}–Cu^{II} complexes of type (**1**) (X---N = aroylhydrazone, thioaroylhydrazone, or salicylideneimine group) have been reported.[5–7] Problems of thiol oxidation, cyclization, *etc.*, were overcome in these thiophenolate systems by protecting the S atom with a dimethylcarbamoyl moiety which could be removed during co-ordination of metal ions.[4,7] We have been particularly interested in obtaining alkanethiolato endogenous groups for comparison with alkanealcoholato *O*-bridging ligands and their Cu^{II} and Ni^{II} complexes, the structural, magnetic, and redox properties of which are known in detail.[8–10] Alkanethiols would normally be expected to be even more prone to adverse redox reactions than the arenethiols in the presence, or absence, of metal ions. Surprisingly, we have found that the diamine precursor to the new ligand shown in complexes of type (**2**), 1,5-diaminopentane-3-thiol,[11] is stable to air when crystallized as the hydrochloride salt and stored at low temperatures. It reacts smoothly with salicylaldehyde and Ni^{II} or Cu^{II} ions without any need for protection. The resulting metal complex, (**2**), represents the first examples of alkanethiolato-bridged metal complexes incorporated within pentadentate binucleating ligands of this general type.‡ The pseudo-square-planar geometry around each metal ion is completed by the N atom of a pyrazolate exogenous bridge. The crystal structure of the nickel complex, described below, clearly shows a pyramidal stereochemistry around the bridging sulphur atom which contrasts with the trigonal-planar geometry commonly,[8] although not always,[9,12] observed in corresponding oxygen-atom bridges.



(**1**)



(**2**)
$[Ni_2L(pz)]$

Experimental

Reagents were laboratory grade and were used without further purification. 1,5-Diaminopentane-3-thiol dihydrochloride was synthesized as described by Murase *et al.*[11] one modification being to synthesize the intermediate 1,5-diaminopentan-3-ol dihydrochloride by the method of Mazurek *et al.*[8] The thiol was stored at 0 °C over silica gel.

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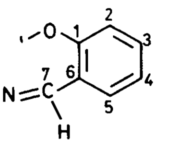
† [*NN'*-3-mercaptopentane-1,5-diylbis(salicylideneiminato)(3−)]-μ-pyrazolato-dinickel(II).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: B.M. = 0.927×10^{-23} A m².

‡ *Note added at proof:* Robson and McKenzie have recently reported binuclear Ni^{II}, Pd^{II}, and Cu^{II} complexes of a new alkanethiolato-bridging ligand, different in design to that shown in (**2**) (C. J. McKenzie and R. Robson, *Inorg. Chem.*, 1987, **26**, 3615).

Syntheses.—[*NN'-3-Mercaptopentane*-1,5-*diylbis*(*salicylideneiminato*)(3 −)]-μ-*pyrazolato-dinickel*(II), [$Ni_2L(pz)$]. A solution of potassium hydroxide (112 mg, 2 mmol) in methanol (1.5 cm^3) was added to a solution of crude 1,5-diaminopentan-3-thiol dihydrochloride (207 mg, 1 mmol) in methanol (2.5 cm^3) with stirring. The resultant mixture was filtered into salicylaldehyde (244 mg, 2 mmol) whereupon a yellow solution was obtained which was stirred for 10 min. The reaction mixture was evaporated under vacuum and the residue dissolved in chloroform. The chloroform was dried over anhydrous magnesium sulphate, filtered, and evaporated under vacuum. The resultant residue was dissolved in methanol (10 cm^3) and a solution of pyrazole (100 mg, 15 mmol) in methanol (5 cm^3) was added. The reaction mixture was filtered into a stirred solution of nickel(II) perchlorate hexahydrate (731 mg, 2 mmol) in methanol (10 cm^3), giving a brown solution. Upon addition of potassium hydroxide (224 mg, 4 mmol) in methanol (5 cm^3), a brown precipitate was obtained. The reaction mixture was evaporated under vacuum and the residue dissolved in chloroform. The chloroform solution (70 cm^3) was washed with water (3 × 50 cm^3), dried over anhydrous magnesium sulphate, filtered and allowed to evaporate slowly at room temperature. Upon reduction to 30 cm^3, ethanol (10 cm^3) was added and the solution began to yield small brown crystals on further evaporation. The crystals were filtered off and dried in air. Brown crystals (72 mg, 14%), m.p. 301—302 °C (Found: C, 50.50; H, 3.95; N, 10.85; S, 6.50. $C_{22}H_{22}N_4Ni_2O_2S$ requires C, 50.95; H, 4.25; N, 10.70; S, 6.10%). U.v.–visible spectrum ($CHCl_3$): 242.5 (sh) (31 200), 256.2br (31 400), 326.4 (8 680), and 386.6 nm (ε 7 210 dm^3 mol^{-1} cm^{-1}). ^1H N.m.r. spectrum ($CDCl_3$, 300 MHz): 7.40 (2 H, d, J = 2.3 Hz, pyrazole protons α to N), 7.37 (2 H, s, imine protons), 7.24—7.15 (2 H, m, phenyl), 7.08—6.98 (2 H, m, phenyl), 6.93—6.78 (2 H, m, phenyl), 6.57—6.42 (2 H, m, phenyl), 5.96 (1 H, t, J = 2.2 Hz, pyrazole proton β to N), 5.63 (1 H, m, CH–S), 3.60—3.52 (2 H, m, CH_2), 3.42—3.30 (2 H, m, CH_2), 3.28—3.17 (2 H, m, CH_2), and 2.04—1.93 (2 H, m, CH_2). ^{13}C N.m.r. spectrum ($CDCl_3$, 75.47 MHz): 164.5 (C^1), 163.9 (C^7), 139.1 (pyrazole carbons α to N), 134.4 (C^3), 132.3 (C^5), 120.9 (C^4), 119.9 (C^6), 114.9 (C^2), 103.5 (pyrazole carbon β to N), 60.6 (CH–S), and 35.1 (CH_2). Mass spectrum: molecular ion peak cluster due to Ni isotopes (main isotopes ^{58}Ni[68.3%], ^{60}Ni[26.1%]) only most intense peak quoted; m/z 522 (M^+ [^{58}Ni ^{58}Ni], 75%), 456 (13), 454 (14), 421 (11), 364 (11), 363 (15), 262 (24), 261 (15), 243 (12), 183 (12), 162 (11), 161 (14), 153 (15), 147 (27), 135 (12), 134 (13), 132 (17), 121 (14), 108 (11), 98 (37), 97 (16), 91 (12), 78 (16), 77 (20), 69 (20), 68 (100), 67 (15), 58 (16), 57 (14), 56 (25), 55 (17), 51 (14). $\mu_{eff.}$(293.1 K) = 0.29 B.M.



[*NN'-3-Mercaptopentane*-1,5-*diylbis*(*salicylideneiminato*)-(3 −)]-μ-*pyrazolato-dicopper*(II) *trihydrate*, [$Cu_2L(pz)$]·$3H_2O$. The ligand solution containing pyrazole, prepared as described above for the dinickel(II) complex, was added to a stirred solution of copper(II) perchlorate hexahydrate (741 mg, 2 mmol) in methanol (10 cm^3). A solution of potassium hydroxide (224 mg, 4 mmol) in methanol (5 cm^3) was added to the resultant solution whereupon a green precipitate was formed. The reaction mixture was evaporated under vacuum and the residue extracted into chloroform. The chloroform solution was washed with water (3 × 50 cm^3), dried over anhydrous magnesium sulphate, filtered and allowed to evaporate slowly at room temperature. A green precipitate formed which was filtered off and dried in air. Green powder (160 mg, 30%), m.p. 216—218 °C (decomp.) (Found: C, 45.05; H, 4.35; Cu, 20.4; N, 10.40; S, 5.80. $C_{22}H_{28}Cu_2N_4O_5S$ requires C, 44.95; H, 4.80; Cu, 21.6; N, 9.55; S, 5.50%). U.v.–visible spectrum ($CHCl_3$): 243.0 (25 000), 273.3 (15 000), 363br (3 700), and 600br nm (ε 430 dm^3 mol^{-1} cm^{-1}). Infrared spectrum (Nujol and hexachlorobutadiene): 3 560m, 3 400m br, 3 050w, 2 920m, 1 620s, 1 600m (sh), 1 540m, 1 470s, 1 450s, 1 410m, 1 380m, 1 350s, 1 330s, 1 280m, 1 210m, 1 180m, 1 160s, 1 140m, 1 090m, 1 070m, 920m, 860w, 770s, 750m, and 730m cm^{-1}. $\mu_{eff.}$(291.2 K) = 1.61 B.M.

Crystallography.—*Crystal data for* [$Ni_2L(pz)$]. $C_{22}H_{22}N_4Ni_2O_2S$, M = 523.9, monoclinic, at 20 °C, a = 9.679(4), b = 8.860(4), c = 24.711(9) Å, β = 98.51(1)°, U = 2 095.8 Å^3, D_m = 1.66(1), D_c = 1.66 g cm^{-3}, Z = 4, F(000) = 1 080, μ = 32.9 cm^{-1} for Cu-K_α radiation (λ = 1.5418 Å). Space group $P2_1/c$. Cell parameters were determined from 24 accurately centred reflections and were calculated by the standard Philips program.

Structure determination. A representative dark red bladed crystal of dimensions 0.12 × 0.12 × 0.04 mm was used for data collection. Intensity measurements were made on a Philips PW1100 diffractometer with graphite monochromated Cu-K_α radiation with $6 < 2\theta \leqslant 110°$, operating in an ω scan mode with a symmetric scan range of $\pm(0.70 + 0.3 \tan\theta)°$ in ω from the calculated Bragg scattering angle at a scan rate of 0.05° s^{-1}. A total of 2 631 unique data were collected, 1 538 of which were considered to be observed [$I \geqslant 3\sigma(I)$]. Three standard reflections monitored every 4 h showed no significant variation in intensity over the data collection period.

Intensity data were processed as described previously.[13] A numerical absorption correction was applied, the maximum and minimum transmission factors being 0.866 and 0.660 respectively. The atomic scattering factors for neutral atoms were taken from ref. 14 and were corrected for anomalous dispersion by using values from ref. 14. All calculations were performed on a VAX11/780 computer. The program used for least-squares refinement was SHELX 76.[15]

The structure was solved by direct methods. Full-matrix least-squares refinement employing anisotropic thermal parameters for Ni and S and isotropic thermal parameters for all other non-hydrogen atoms [a single isotropic thermal parameter for hydrogen (hydrogen in geometrically idealized positions: C–H 1.08 Å)] reduced R and R' to 0.065 and 0.065, respectively, at convergence, where $R' = \Sigma w^{\frac{1}{2}}(||F_o| - |F_c||)/\Sigma w^{\frac{1}{2}}|F_o|$, and $w = [\sigma^2(F_o)]^{-1}$. Final atomic parameters are given in Table 1, bond lengths and angles in Table 2. The Figure shows the atomic labelling scheme used. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Physical Measurements.—Variable-temperature magnetic susceptibility measurements were obtained using an Oxford Instruments Faraday balance as described previously.[8] Proton and ^{13}C n.m.r. spectra were measured on a Brüker AM300 spectrometer, and u.v.–visible spectra on an Hitachi 150-20 spectrometer.

Results and Discussion

Synthesis of NN'-3-*Mercaptopentane*-1,5-*diylbis*(*salicylideneimine*) (H_3L) *and the Metal Complexes*, [$M_2L(pz)$], *where* M = Ni^{II} *or* Cu^{II}.—1,5-Diaminopentane-3-thiol was prepared from 1,5-diaminopentan-3-ol in a multistep synthesis as described by Murase *et al.*[11] It was isolated as the dihydrochloride salt which was stored at low temperature in a dry environment. The pentadentate ligand H_3L was prepared *in situ*

Table 1. Positional parameters for $[Ni_2L(pz)]$, with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni(1)	0.559 4(2)	0.216 8(2)	0.023 9(1)	C(14)	0.218 5(12)	0.256 7(12)	0.238 5(4)
Ni(2)	0.423 6(2)	0.279 0(2)	0.145 9(1)	C(15)	0.123 2(12)	0.233 8(13)	0.276 4(4)
S	0.425 7(3)	0.364 1(4)	0.063 1(1)	C(16)	0.151 2(12)	0.139 6(13)	0.319 2(5)
C(1)	0.736 5(11)	0.134 5(12)	−0.054 3(4)	C(17)	0.277 1(13)	0.064 4(13)	0.327 9(5)
C(2)	0.875 2(12)	0.111 5(12)	−0.065 0(4)	C(18)	0.374 9(12)	0.083 6(13)	0.292 9(4)
C(3)	0.897 6(13)	0.095 2(13)	−0.118 5(5)	C(19)	0.347 4(11)	0.179 5(11)	0.247 1(4)
C(4)	0.793 2(13)	0.101 6(13)	−0.162 7(5)	C(20)	0.801 9(11)	0.166 4(12)	0.109 7(4)
C(5)	0.657 4(13)	0.119 9(12)	−0.152 1(5)	C(21)	0.828 8(13)	0.143 0(13)	0.165 0(4)
C(6)	0.628 5(11)	0.139 0(12)	−0.097 8(4)	C(22)	0.705 2(12)	0.166 4(12)	0.184 6(5)
C(7)	0.486 1(11)	0.158 8(12)	−0.089 8(4)	N(1)	0.441 8(9)	0.193 4(9)	−0.044 2(3)
C(8)	0.286 5(11)	0.194 2(12)	−0.047 8(4)	N(2)	0.253 0(9)	0.376 7(10)	0.152 9(4)
C(9)	0.230 6(13)	0.339 7(12)	−0.028 7(4)	N(3)	0.664 5(9)	0.202 6(9)	0.093 7(3)
C(10)	0.244 6(15)	0.345 0(16)	0.033 9(5)	N(4)	0.604 5(9)	0.200 6(10)	0.141 5(3)
C(11)	0.151 9(13)	0.444 8(15)	0.056 2(5)	O(1)	0.718 6(7)	0.151 8(8)	−0.002 7(3)
C(12)	0.205 3(14)	0.500 0(15)	0.114 3(5)	O(2)	0.441 7(7)	0.195 6(8)	0.215 3(3)
C(13)	0.183 0(12)	0.354 9(12)	0.192 7(4)				

Table 2. Selected bond lengths (Å) and angles (°) for $[Ni_2L(pz)]$, with e.s.d.s in parentheses

Ni(1)–S	2.165(4)	Ni(2)–N(4)	1.901(9)	C(8)–C(9)	1.50(2)	O(2)–C(19)	1.30(1)
Ni(2)–S	2.182(3)	Ni(1)–Ni(2)	3.507(3)	C(9)–C(10)	1.53(2)	N(3)–N(4)	1.39(1)
Ni(1)–O(1)	1.855(8)	S–C(10)	1.80(1)	C(10)–C(11)	1.43(2)	N(3)–C(20)	1.37(1)
Ni(1)–N(1)	1.897(8)	O(1)–C(1)	1.32(1)	C(11)–C(12)	1.53(2)	N(4)–C(22)	1.37(1)
Ni(1)–N(3)	1.874(8)	N(1)–C(7)	1.30(1)	N(2)–C(12)	1.48(1)	C(20)–C(21)	1.37(1)
Ni(2)–O(2)	1.851(7)	N(1)–C(8)	1.49(1)	N(2)–C(13)	1.29(1)	C(21)–C(22)	1.37(2)
Ni(2)–N(2)	1.859(9)						
S–Ni(1)–N(1)	98.2(3)	N(3)–Ni(1)–O(1)	86.5(3)	N(2)–Ni(2)–N(4)	173.9(4)	Ni(1)–S–C(10)	112.0(5)
S–Ni(1)–N(3)	84.7(3)	S–Ni(2)–N(2)	93.3(3)	N(2)–Ni(2)–O(2)	93.6(4)	Ni(2)–S–C(10)	101.5(5)
S–Ni(1)–O(1)	158.3(2)	S–Ni(2)–N(4)	86.3(3)	N(4)–Ni(2)–O(2)	86.9(3)	Ni(1)–N(3)–N(4)	123.0(6)
N(1)–Ni(1)–N(3)	169.1(4)	S–Ni(2)–O(2)	173.2(3)	Ni(1)–S–Ni(2)	107.5(1)	Ni(2)–N(4)–N(3)	123.2(6)
N(1)–Ni(1)–O(1)	94.2(3)						

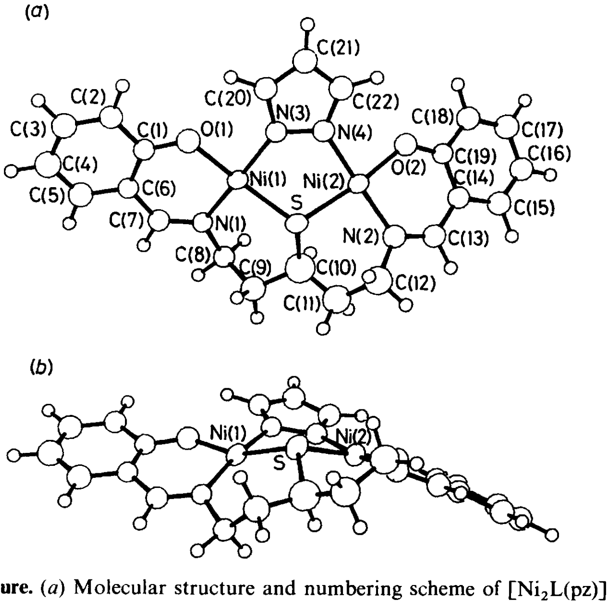


Figure. (*a*) Molecular structure and numbering scheme of $[Ni_2L(pz)]$ (**2**) viewed from above. Thermal ellipsoids have been drawn at the 50% probability level. (*b*) A different perspective of $[Ni_2L(pz)]$ showing the conformation of the whole binuclear framework and the pyramidal nature of the bridging sulphur atom

in methanol by reacting salicylaldehyde with the dihydrochloride salt in the presence of potassium hydroxide. The ligand was not isolated from solution but used directly in the synthesis of the metal complexes.

The binuclear *S*-bridged complexes $[Ni_2L(pz)]$ and $[Cu_2L(pz)]\cdot 3H_2O$ were obtained by reaction of the ligand solution with two mole equivalents of the metal perchlorate in the presence of potassium hydroxide and pyrazole. The dinickel(II) and dicopper(II) complexes were isolated as brown crystals and a green powder, respectively. Their i.r. spectra are similar, although the spectrum for the copper complex shows bands at 3 560 cm^{-1} and 3 400 cm^{-1} due to water, ν(OH), vibrations.

Spectral and Magnetic Properties of $[M_2L(pz)]$ *Complexes.*—$[Ni_2L(pz)]$ is diamagnetic which is indicative of a planar geometry around the Ni^{II} ions. The ^1H and ^{13}C n.m.r. spectra of the complex in $CDCl_3$ are well resolved and similar to those of analogous *O*-bridged dinickel(II) complexes.[10] The ^1H n.m.r. spectrum shows aromatic resonances in the region 7.2—6.4 p.p.m. with distinct resonances at 5.96 p.p.m. due to the coordinated pyrazolate ring. A line at 7.37 p.p.m. is assigned to the two CH=N protons being in identical environments. The CH_2 protons of the pentanethiol moiety were found to give four distinct resonances at *ca.* 3.6, 3.4, 3.2, and 1.9 p.p.m., each of which show multiple splitting. This indicates that the CH_2 groups are in non-equivalent environments which is in agreement with the crystal structure of the complex (described below and shown in the Figure). Similarly, in the ^{13}C n.m.r. spectrum, the CH_2 resonances appear as a broad signal at 35.1 p.p.m. All other ^{13}C resonances were resolved and assignable (Experimental section).

U.v.–visible spectra of chloroform solutions of $[Ni_2L(pz)]$ and $[Cu_2L(pz)]\cdot 3H_2O$ show strong intraligand π–π* transitions in the region 243—273 nm. Other bands of lower intensity in the region 320—390 nm are due to charge-transfer transitions. A band at 600 nm in the spectrum of the copper complex is due to a *d–d* transition; the same band in the *O*-bridged analogue occurs at 588 nm.[9]

A magnetic moment, per Cu, of 1.61 B.M. for $[Cu_2L(pz)]\cdot 3H_2O$ is indicative of weak antiferromagnetic exchange occurring between the Cu^{II} ions. This is confirmed by the gradual decrease to 1.28 B.M. observed when the temperature was lowered to 4.2 K. However, the μ/T data could not be fitted well to the Bleaney–Bowers model,[16] possibly because the Cu^{II} ions, within the binuclear moiety, have slightly different geometries. Nevertheless, the weak antiferromagnetic coupling is of similar magnitude to that recently observed[7] in some thiophenolate-bridged derivatives, (**1**), and is much weaker than that observed in the analogous *O*-bridged *NN'*-3-hydroxypentane-1,5-diylbis(salicylideneimine)–copper complex which is so strongly coupled it is diamagnetic at room temperature.[9] This difference is probably due primarily to the different geometries adopted by the bridging-*S* and -*O* atoms, the former being presumably pyramidal in nature by comparison to the crystal structure of the nickel complex, while the latter is trigonal planar and more conducive to good overlap with the Cu $d_{x^2-y^2}$ orbitals.[9]

Crystal and Molecular Structure of $[Ni_2L(pz)]$.—Positional parameters and bond lengths and angles are given in Tables 1 and 2. Two perspectives of the binuclear molecule are shown in Figure 1. It can be seen that the two NiN_2OS chromophores are not coplanar nor are the two salicylideneimine rings. This is presumably a result of the steric constraints imposed by a combination of the μ-pyrazolate bridging group and the size of the bridging S atom. While the geometry around each Ni is approximately square planar, that around Ni(1) is more distorted; compare O(1)–Ni(1)–S, 158.3(2)° with O(2)–Ni(2)–S, 173.2(3)°. The Ni–S bond lengths are typical of those in mononuclear chelated complexes[17] and marginally shorter than those in the bridging Ni–S bonds of homoleptic dimers such as $[Ni_2(SEt)_6]^{2-}$[18] and $[Ni_2(SCH_2CH_2S)_3]^{2-}$.[19] The former contains two planar (and nearly coplanar) NiS_4 chromophores, the latter has a dihedral angle of 118° between the NiS_4 chromophores. The Ni(1) ··· Ni(2) distance in the present complex, 3.507(3) Å, and the Ni(1)–S–Ni(2) angle, 107.5(1)°, are intermediate between those recently observed in Cu^{II}–Cu^{II} and Pd^{II}–Pd^{II} thiophenolate-bridged complexes of type (**1**).[6,7] One notable feature of the structure is the pyramidal nature of the bridging-*S* atom, which, on the basis of the small number of related structures, appears to be characteristic of thiophenolate or alkanethiolate S atoms. This is perhaps not surprising in view of the orbitals employed by the S atom and by its size. Indeed, Robson and co-workers[5] anticipated these structural features many years before crystal structures of these types of molecules were available.

Acknowledgements

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