DALTON

Phosphine-participated formation and crystal structures of nickel complexes with 2-sulfanylphenol and phosphine ligands †

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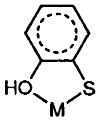
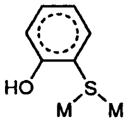
Neutral tri- and mono-nuclear complexes $[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$ **1** and $[Ni(OC_6H_4S)(PMe_2Ph)_2]$ **2** of 2-sulfanylphenol were obtained in the presence of a phosphine in EtOH solutions, and their crystal structures determined. Complex **1** is made up of three nickel ions chelated and bridged by two $OC_6H_4S^{2-}$ dianions in O_bS_t fashion and two $HOC_6H_4S^-$ monoanions in HO_tS_b fashion, where the central nickel(II) atom has an elongated octahedral geometry whereas the two at the sides have square-planar surroundings. In **2** the nickel(II) atom is located in a square-planar environment, chelated by a $OC_6H_4S^{2-}$ dianion in O_tS_t mode. Complex **1** is paramagnetic and its magnetic behaviour is explained by single-ion anisotropy.

Metal complexes with mixed phosphine and thiolate ligands have been actively investigated in the last few years.[1–6] For transition-metal thiolates it is found that under suitable conditions the presence of a phosphine favours the formation of multinuclear complexes involving bidentate thiolate and monodentate tertiary phosphine ligands.[7–10] This research in recent years has resulted in a broad class of compounds with an astounding degree of complexity and nuclearity.[11]

2-Sulfanylphenol is a versatile bidentate compound which plays a key role in the design of polymetallic systems with phosphine participation.[8,11] It can form the monoanion $HOC_6H_4S^-$ or dianion $OC_6H_4S^{2-}$ in different circumstances, chelating or/and bridging metal ions in various modes shown as follows: HO_tS_t **I**, HOS_b **II**, HO_tS_b **III**, O_tS_t **IV**, O_tS_b **V**, O_bS_t **VI**, O_bS_b-B **VII** and O_bS_b-T **VIII** (b stands for bridge, t for terminal, B for binuclear and T for trinuclear). All the bridging modes except **III** have been observed in transition-metal compounds and/or phosphine-participated cobalt clusters of 2-sulfanylphenol.[8,12] In order to extend this work, we are engaged in the investigation of nickel complexes of this compound with phosphine participation. It has been found that $[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$ exhibits a different co-ordination behaviour from those of the corresponding cobalt complexes and that the thiolate anion displays a new bridging mode, HO_tS_b **III**. We report here the syntheses and crystal structures of two nickel complexes, $[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$ **1** and $[Ni(OC_6H_4S)(PMe_2Ph)_2]$ **2** together with a description of the magnetic behaviour of **1**.



I



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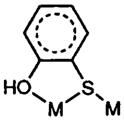

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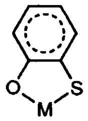

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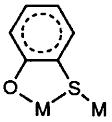

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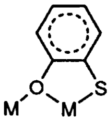

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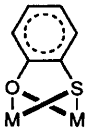
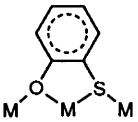


VII



VIII

Experimental

All operations were carried out under a dinitrogen atmosphere with a Schlenk-type apparatus. 2-Sulfanylphenol, tri-*n*-butylphosphine, and dimethylphenylphosphine were obtained from Merck-Schuchardt, and $NiCl_2\cdot 6H_2O$ from Shanghai. Absolute ethanol was flushed with pure dinitrogen for 2–3 min before use. Sodium ethoxide was prepared by dissolving sodium metal in dry ethanol and then evaporating the solvent and drying under reduced pressure.

Synthesis

$[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$ 1. To a solution (30 cm^3) of absolute EtOH containing NaOEt (0.14 g, 2 mmol) was added HOC_6H_4SH-2 (0.1 cm^3, 1 mmol) and $PBu^n{}_3$ (0.20 cm^3, 1 mmol) with vigorous stirring. The resulting solution turned brown-yellow after a EtOH solution (5 cm^3) of $NiCl_2\cdot 6H_2O$ (0.245 g, 1 mmol) was added with stirring. After 1 h the solution was filtered and allowed to stand at 4 °C for several days to give well shaped dark brown crystals of complex **1**. Yield: 69% (Found: C, 53.50; H, 7.45; Ni, 15.30; P, 5.40; S, 10.50. Calc. for $C_{52}H_{84}Ni_3O_6P_2S_4$: C, 53.30; H, 7.25; Ni, 15.05; P, 5.30; S, 10.95%). IR (KBr, cm^{-1}): 410w, 440w, 457m, 652m, 679m, 692m, 721m, 746s, 873m, 907m, 1026m, 1065m, 1092m, 1238m, 1267s, 1379m, 1410m, 1460s, 1564m, 2870m, 2930s, 2957s, 3053m, 3435m and 3586w. UV (Me_2SO, cm^{-1}): 15 625, 21 280, 31 250 and 33 900.

$[Ni(OC_6H_4S)(PMe_2Ph)_2]$ 2. To a solution of $NiCl_2\cdot 6H_2O$ (0.245 g, 1 mmol) in absolute EtOH (30 cm^3) was added PMe_2Ph (0.30 cm^3, 2 mmol) with stirring, resulting in a yellow solution. After stirring for a while, NaOEt (0.14 g, 2 mmol) and HOC_6H_4SH-2 (0.1 cm^3, 1 mmol) dissolved in absolute EtOH

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† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24} \text{ J T}^{-1}$.

(10 cm^3) were added. The deep red-yellow solution was filtered after stirring for 30 min, and kept at 4 °C for several days to give well shaped parallelepiped cubic crystals. Yield: 54% (Found: C, 57.40; H, 5.90; Ni, 12.70; P, 13.65; S, 6.65. Calc. for $C_{22}H_{26}NiOP_2S$: C, 57.55; H, 5.70; Ni, 12.80; P, 13.50; S, 6.95%). IR (KBr, cm^{-1}): 442w, 455w, 689w, 748m, 850m, 1026m, 1112m, 1273s, 1460s, 1574s, 2950m and 3052w. UV (Me_2SO, cm^{-1}): 16 670, 25 000 and 32 260.

Crystal structure determinations

Suitable single crystals of complexes **1** and **2** were mounted on a glass fibre and data collections were performed at 293 K on a Rigaku RAXIS diffractometer[13] and a Rigaku AFC7R four-circle diffractometer, respectively, using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). The crystal data, data collection and structure refinement parameters are summarized in Table 1.

The coordinates of the metal atoms were determined by the direct method and the remaining non-hydrogen atoms located from successive Fourier-difference syntheses. The structures were refined on F by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms. For complex **1** the atoms C(15), C(16), C(15′), C(16′), O(3) and O(3′) have occupancy factors of 0.5. The solvent ethanol molecule is two-fold disordered, so that each hydroxyl O atom is represented by two half-oxygen atoms, *i.e.* O(3) and O(3′). All calculations were performed on a IBM PC/486 computer with the Siemens SHELXTL PLUS program package.[14] Atomic scattering factors were taken from ref. 15. The atomic coordinates of the non-hydrogen atoms for complexes **1** and **2** are listed in Tables 1 and 2, respectively, selected bond distances and angles in Table 3.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Physical measurements

Infrared spectra were recorded on a Perkin-Elmer 577 spectrophotometer, ^1H and ^{31}P NMR spectra on a Bruker AM500 spectrometer with $SiMe_4$ as the internal standard and 85% H_3PO_4 as external standard, respectively. Powder EPR spectra were recorded on a Bruker 2000-SRC spectrometer. Cyclic voltammetric measurements were performed on a DHZ-1 electrochemical apparatus equipped with an X-Y recorder in a three-electrode cell with platinum working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. The supporting electrolyte was $NBu^n{}_4BF_4$ (0.1 mol dm^{-3}) and scan rate 100 mV s^{-1}. Variable-temperature magnetic susceptibilities in the temperature range 1.5–300 K were measured on a model CF-1 superconducting extracting sample magnetometer at a magnetic field of 5.0 T with the powdered samples kept in capsules for weighing. A correction for the diamagnetism of compound **1** was estimated from Pascal's constants to be -508×10^{-6} cm^3 mol^{-1}.

Results and Discussion

Synthesis

The trinuclear complex **1** was synthesized from the reaction of $NiCl_2 \cdot 6H_2O$, HOC_6H_4SH-2, NaOEt and $PBu^n{}_3$ in 1:1:2:1 molar ratio with ethanol as solvent under anaerobic conditions, while the mononuclear complex **2** was obtained at a molar ratio of 1:1:2:2 by using PMe_2Ph as the phosphine. When triethylamine was used as the base to remove the protons of the thiol the compound $[NEt_3H][Ni(OC_6H_4S)(HOC_6H_4S)(PBu^n{}_3)]$ **3** was isolated, unexpectedly.[16]

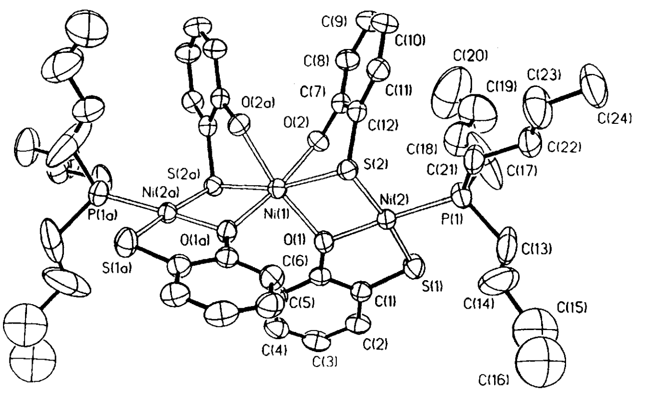

Fig. 1 Structure of compound **1** with the atomic labelling scheme

Structures

$[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2] \cdot 2EtOH$ 1. The structure of complex **1** with the atomic labelling scheme is depicted in Fig. 1. The molecule which lies on a crystallographic C_2 axis may be viewed as a Ni^{2+} ion, to which two $Ni(OC_6H_4S)(HOC_6H_4S)(PBu^n{}_3)$ fragments are *cis* bonded. As a result, the sulfur atoms S(2) and S(2a) in the $HOC_6H_4S^-$ anions and the oxygen atoms O(1) and O(1a) in the $OC_6H_4S^{2-}$ dianions serve as bridging groups.

Complex **1** is made up of three nickel(II) ions bridged by two dianions in O_bS_t **VI** fashion and two anions in HO_tS_b **III** fashion. The $Ni_3O_4S_4P_2$ core is built up from an octahedral NiO_4S_2 unit in the centre, and two edge-linked square-planar $NiOS_2P$ units at both sides, connected in a *cis* fashion with respect to the central Ni(1) site. The arrangement of the three nickel atoms is quasi-linear with the angle Ni(2)–Ni(1)–Ni(2a) being 148.9°, similar to that of dithiolate complexes $[Ni_3(edt)_4]^{2-}$ (edt = ethane-1,2-dithiolate) and $[Ni_3(SCH_2C_6H_4CH_2S\text{-}2)_4]^{2-}$.[17] However, the $Ni_3O_4S_4P_2$ framework is different from the corresponding moiety in the cyclic trinuclear complex $[Ni_3(hcndt)_3(PPh_3)_3]$ (hcndt = hexachloronaphthalene-1,8-dithiolate)[5] in which the S_6 of the $Ni_3S_6P_3$ core is in a trigonal-prismatic arrangement and the Ni_3 is in an equilateral triangle with the angle Ni–Ni–Ni being 60.0°.

The repeating asymmetric unit contains two nickel centres of non-identical geometries. Atom Ni(1) has an elongated octahedral environment, whereas Ni(2) has distorted square-planar surroundings. The equatorial plane of Ni(1) is defined by O(2) and O(2a) from two $HOC_6H_4S^-$ anions, and O(1) and O(1a) from two $OC_6H_4S^{2-}$ dianions which are bound to Ni(2) and Ni(2a), respectively. The two axial co-ordination sites are occupied by S(2) and S(2a) which are bound to Ni(2) and Ni(2a), respectively. The co-ordination plane of Ni(2) is composed of atoms O(1), S(1), P(1) and S(2), and Ni(2) is displaced out of the plane by 0.0016 Å.

The Ni • • • Ni distance is 3.122 Å and thus outside the range for direct metal–metal interaction. The distances involving bridging S_b [Ni(1)–S(2) 2.422(1) and Ni(2)–S(2) 2.271(1) Å] are significantly longer than that of terminal S_t [Ni(2)–S(1) 2.161(2) Å], similar to what is found in other nickel thiolate or mixed thiolate and phosphine compounds.[9,17] The Ni–S_b distance [2.422(1) Å] within a Ni–O–C–C–S five-membered chelate ring is much longer than that of the ring outside [2.271(1) Å] due to Ni(1)–S(2) and Ni(1)–S(2a) occupying the axial positions whereas Ni(2)–S(2) and Ni(2a)–S(2a) are in the square planes, contrary to the situation in other phosphine-participated thiolate compounds,[7–10] while the Ni–O_b distance [Ni(2)–O(1) 1.897(4) Å] inside the five-membered chelate ring is much shorter than that outside [Ni(1)–O(1) 2.027(4) Å], similar to the corresponding distances in other complexes with mixed phosphines and HOC_6H_4SH-2.[8]

The five-membered chelate ring Ni(2)S(1)C(1)C(6)O(1) is planar with Ni(2) deviating only by 0.0164 Å, whereas the ring Ni(1)O(2)C(7)C(12)S(2) is non-planar with Ni(1) displaced out of the plane O(2)C(7)C(12)S(2) by 1.028 Å. The Ni–O–C angles (114.7–131.3°) are much larger than the Ni–S–C angles (94.5–104.3°) due to the different orbitals for bonding of the O and S atoms. The oxygen-donor atoms are sp^2 hybridized, while the bonding orbitals of the sulfur-donor atoms are mainly of p character.[12] The distances O(2) · · · O(3) and O(2) · · · O(3′) are 2.620 and 2.605 Å, respectively, indicating strong hydrogen bonds between the thiolate anions and solvate ethanol molecules.

$[Ni(OC_6H_4S)(PMe_2Ph)_2]$ 2. The structure of complex **2** with the atom labelling scheme is displayed in Fig. 2. The neutral mononuclear molecule is built up from a nickel atom bonded to two PMe_2Ph and a $OC_6H_4S^{2-}$ dianion in O,S_t **IV** mode, where the nickel has approximately square-planar surroundings. It is displaced out of the co-ordination plane by 0.190 Å. The whole molecule has no symmetry due to the non-equivalent O and S atoms in $OC_6H_4S^{2-}$. The Ni–O, Ni–S and Ni–P distances for this compound are similar to those for the Ni(2) centre in **1**.

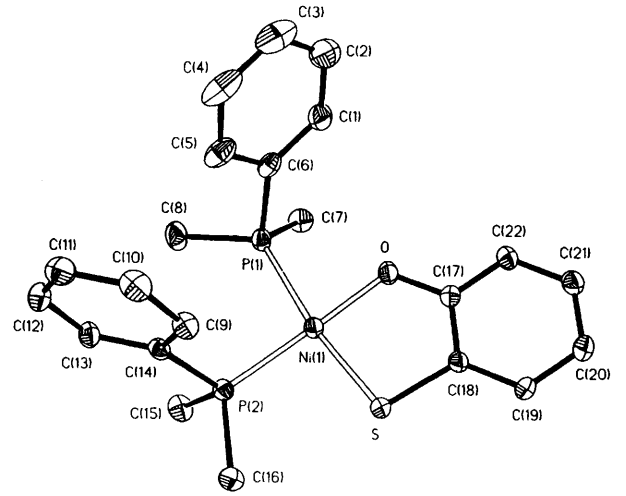

Fig. 2 Structure of compound **2** with the atomic labelling scheme

Spectral data

The EPR spectrum of a polycrystalline powdered sample of complex **1** at room temperature consists of two peaks with $g_{\parallel}$ = 2.18 and $g_{\perp}$ = 2.03, which is characteristic of an octahedral nickel ion with $S = 1$.[18] The spectrum does not change on lowering the temperature, other than to increase in intensity with no hyperfine splitting.

Cyclic voltammetric studies reveal that complexes **1** and **2** have only one irreversible oxidation wave at 0.50 and 0.62 V, respectively, similar to the electrochemical behaviours of other nickel thiolates.[19]

The ^1H NMR spectrum of compound **1** in $(CD_3)_2SO$ shows a singlet at δ 11.81 assignable to the hydroxyl group of the bridging ligand $HOC_6H_4S^-$. This signal is absent in the spectrum of compound **2** in which the thiolate is present in the form of the dianion. The proton resonances of the benzene ring are found mainly in the range δ 6.2–7.3 as a complicated multiplet. For compound **1** there is a broad peak centred at δ 4.15 originating from the OH protons of the solvate EtOH molecules which are involved in hydrogen bonding. The ^{31}P NMR spectrum of **1** shows a strong signal at δ 10.36 and a weak one at δ 47.17. The former became weaker, whereas the latter became stronger when the sample was left in the air. After several days the first peak had disappeared. The spectrum of compound **2** gives two signals at δ 32.4 and 33.3 due to the two inequivalent bonded P atoms.

Magnetic behaviour

The magnetic behaviour of compound **1** in the range 1.5–300 K is shown in Fig. 3 in the form of the temperature dependence of the molar susceptibility χ_m and $1/\chi_m$. The molar susceptibility continues to increase down to the lowest temperature measured. However, using the Curie–Weiss equation $\chi_m = 2Ng^2\beta^2/3k(T - \theta)$ to fit the magnetic data reveals a deviation from Curie-like behaviour. The Curie–Weiss parameters are $C = 1.17\ cm^3\ K\ mol^{-1}$ ($C = 2Ng^2\beta^2/3k$) and $\theta = -5.3$ K. The value of the Curie constant implies a g factor of 2.16, which is normal for a nickel(II) ion in an octahedral environment.

In the temperature range 300–7 K the effective moment μ_{eff} [$\mu = 2.828\ (\chi_m T)^{\frac{1}{2}}$] decreases slowly from 3.20 μ_B at 300 K to 2.50 μ_B at 7 K. Below 7 K μ_{eff} drops rapidly to 2.0 μ_B at 4.0 K

Table 1 Summary of crystal data, data collection and structure refinement of complexes **1** and **2**

	1	**2**
Formula	$C_{52}H_{84}Ni_3O_6P_2S_4$	$C_{22}H_{26}NiOP_2S$
M	1170.8	458.9
Colour and habit	Black-brown prism	Yellow parallelepiped
Crystal size/mm	0.15 × 0.20 × 0.30	0.20 × 0.24 × 0.42
System	Monoclinic	Monoclinic
Space group	$P2/c$	$P2_1/n$
a/Å	15.943(1)	12.127(2)
b/Å	9.615(1)	13.415(3)
c/Å	19.650(1)	14.413(3)
β/°	93.49(1)	108.47(3)
U/Å^3	3006.6(15)	2224.1(1.0)
Z	2	4
D_c/g cm^{-3}	1.292	1.374
μ(Mo-Kα)/cm^{-1}	11.64	11.2
$F(000)$	1240	960
Independent reflections	5768	4371
Observed reflections	2974 [$\lvert F_o\rvert \geqslant 10\sigma(\lvert F_o\rvert)$]	3610 [$\lvert F_o\rvert \geqslant 4\sigma(\lvert F_o\rvert)$]
R^a	0.048	0.037
R'^b	0.059	0.058
No. of variables	311	209
S (goodness of fit)	0.84	1.44
Largest and mean Δ/σ	0.011, 0.001	0.006, 0.003
Residual extrema/e Å^{-3}	+0.67 to −0:37	+0.57 to −0.32
R_{int}	0.038	0.039

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R' = [\Sigma w(|F_o| - F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w^{-1} = \sigma^2(F_o) + gF^2$; g = 0.00003 for **1** and 0 for **2**.

Table 2 Atomic coordinates for compound **1**

Atom	*x*	*y*	*z*
Ni(1)	0	0.017 17(11)	0.250 00(8)
Ni(2)	0.187 82(4)	0.099 99(8)	0.237 64(3)
S(1)	0.261 7(1)	0.212 0(2)	0.315 5(1)
O(1)	0.089 4(2)	0.158 7(4)	0.279 1(2)
C(1)	0.178 1(3)	0.280 8(5)	0.359 3(3)
C(2)	0.189 1(4)	0.369 5(5)	0.414 9(3)
C(3)	0.119 4(4)	0.421 0(5)	0.445 0(3)
C(4)	0.039 8(4)	0.388 0(6)	0.419 5(3)
C(5)	0.027 0(4)	0.301 5(5)	0.363 6(3)
C(6)	0.096 9(3)	0.245 1(5)	0.333 7(2)
S(2)	0.098 2(1)	−0.011 6(2)	0.161 8(1)
O(2)	0.077 9(2)	−0.148 7(4)	0.292 6(2)
C(7)	0.104 9(3)	−0.243 2(5)	0.245 1(3)
C(8)	0.119 3(4)	−0.380 5(5)	0.260 7(3)
C(9)	0.144 7(4)	−0.469 6(6)	0.211 3(3)
C(10)	0.152 7(4)	−0.426 5(5)	0.146 3(3)
C(11)	0.138 3(4)	−0.285 3(5)	0.129 4(3)
C(12)	0.115 9(3)	−0.189 6(5)	0.178 8(3)
P(1)	0.303 6(1)	0.037 2(2)	0.193 8(1)
C(13)	0.379 1(4)	0.178 1(6)	0.185 9(5)
C(14)	0.349 3(6)	0.288 2(7)	0.142 8(6)
C(15)	0.415 5(7)	0.420 9(7)	0.153 3(7)
C(16)	0.398 7(8)	0.514 6(8)	0.090 5(7)
C(15′)	0.391 9(8)	0.404 2(7)	0.108 4(7)
C(16′)	0.411 1(8)	0.532 8(7)	0.153 0(7)
C(17)	0.361 4(5)	−0.088 5(7)	0.244 1(5)
C(18)	0.333 0(5)	−0.171 0(7)	0.290 9(5)
C(19)	0.380 8(6)	−0.273 0(7)	0.333 3(5)
C(20)	0.346 0(7)	−0.354 6(8)	0.373 8(7)
C(21)	0.294 5(4)	−0.035 0(6)	0.108 9(3)
C(22)	0.374 0(4)	−0.075 9(6)	0.074 6(3)
C(23)	0.358 1(5)	−0.138 9(7)	0.005 1(4)
C(24)	0.432 5(5)	−0.185 0(7)	−0.031 3(4)
O(3)	0.075 9(5)	−0.245 5(6)	0.417 3(3)
C(25)	0.093 8(6)	−0.166 4(7)	0.474 8(5)
C(26)	0.124 2(6)	−0.031 5(7)	0.456 4(4)
O(3′)	0.175 4(6)	−0.072 2(7)	0.397 1(5)

Atoms C(15), C(16), C(15′), C(16′), O(3) and O(3′) have half occupancy.

Table 3 Atomic coordinates for compound **2**

Atom	*x*	*y*	*z*
Ni	0.1975(1)	0.9815(1)	0.0067(1)
P(1)	0.1745(1)	0.8395(1)	−0.0758(1)
C(1)	0.3465(2)	0.7006(2)	0.0197(2)
C(2)	0.4515(1)	0.6506(3)	0.0344(2)
C(3)	0.5232(2)	0.6758(4)	−0.0209(1)
C(4)	0.4898(3)	0.7511(3)	−0.0911(2)
C(5)	0.3848(3)	0.8012(2)	−0.1058(1)
C(6)	0.3131(1)	0.7759(3)	−0.0504(1)
C(7)	0.0816(3)	0.7577(2)	−0.0338(2)
C(8)	0.1108(4)	0.8238(3)	−0.2076(2)
P(2)	0.1571(1)	1.0804(1)	−0.1170(1)
C(9)	0.3752(1)	1.0659(2)	−0.1329(1)
C(10)	0.4581(1)	1.0486(1)	−0.1797(2)
C(11)	0.4229(1)	1.0275(2)	−0.2796(1)
C(12)	0.3047(1)	1.0237(1)	−0.3327(1)
C(13)	0.2219(1)	1.0410(2)	−0.2860(2)
C(14)	0.2571(2)	1.0622(2)	−0.1861(1)
C(15)	0.0099(2)	1.0695(3)	−0.2002(2)
C(16)	0.1679(3)	1.2146(2)	−0.0959(1)
S	0.2305(1)	1.1059(1)	0.1063(1)
O	0.2338(2)	0.8936(2)	0.1120(1)
C(17)	0.2659(2)	0.9319(1)	0.2034(1)
C(18)	0.2706(1)	1.0352(2)	0.2150(1)
C(19)	0.3047(1)	1.0767(1)	0.3086(2)
C(20)	0.3341(1)	1.0148(2)	0.3906(1)
C(21)	0.3294(2)	0.9115(1)	0.3790(1)
C(22)	0.2953(2)	0.8700(1)	0.2854(1)

Table 4 Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound **1**

Ni(1)–O(1)	2.027(4)	Ni(2)–S(2)	2.271(1)
Ni(1)–O(2)	2.159(4)	Ni(2)–S(1)	2.161(2)
Ni(1)–S(2)	2.422(1)	Ni(2)–P(1)	2.169(2)
Ni(2)–O(1)	1.897(4)		
O(1)–Ni(1)–S(2)	78.7(1)	O(1)–Ni(1)–O(2)	90.5(1)
S(2)–Ni(1)–O(2)	79.1(1)	O(1)–Ni(1)–O(1a)	95.7(2)
S(2)–Ni(1)–O(1a)	110.4(1)	O(2)–Ni(1)–O(1a)	169.5(1)
O(1)–Ni(1)–S(2a)	110.4(1)	S(2)–Ni(1)–S(2a)	166.9(1)
O(2)–Ni(1)–S(2a)	91.1(1)	O(1a)–Ni(1)–S(2a)	78.7(1)
O(1)–Ni(1)–O(2a)	169.5(1)	S(2)–Ni(1)–O(2a)	91.1(1)
O(2)–Ni(1)–O(2a)	84.8(2)	O(1a)–Ni(1)–O(2a)	90.5(1)
S(2a)–Ni(1)–O(2a)	79.1(1)	S(1)–Ni(2)–O(1)	88.7(1)
S(1)–Ni(2)–S(2)	174.0(1)	O(1)–Ni(2)–S(2)	85.3(1)
S(1)–Ni(2)–P(1)	88.8(1)	O(1)–Ni(2)–P(1)	177.5(1)
S(2)–Ni(2)–P(1)	97.1(1)	Ni(2)–S(1)–C(1)	97.9(2)
Ni(1)–O(1)–Ni(2)	105.4(2)	Ni(1)–O(1)–C(6)	131.3(3)
Ni(2)–O(1)–C(6)	119.1(3)	Ni(1)–S(2)–Ni(2)	83.4(1)
Ni(1)–S(2)–C(12)	94.5(2)	Ni(2)–S(2)–C(12)	104.3(2)
Ni(1)–O(2)–C(7)	114.7(3)	Ni(2)–P(1)–C(13)	114.1(3)
Ni(2)–P(1)–C(17)	113.1(3)	Ni(2)–P(1)–C(21)	116.9(2)

Compound **2**

Ni–P(1)	2.216(1)	Ni–P(2)	2.152(1)
Ni–O	1.861(2)	Ni–S	2.154(1)
P(1)–Ni–P(2)	97.4(1)	P(1)–Ni–S	171.4(1)
P(2)–Ni–S	91.1(1)	P(1)–Ni–O	81.4(1)
P(2)–Ni–O	178.6(1)	S–Ni–O	90.1(1)
Ni–P(1)–C(6)	110.1(1)	Ni–P(1)–C(7)	109.2(1)
Ni–P(1)–C(8)	126.8(1)	Ni–P(2)–C(14)	110.8(1)
Ni–P(2)–C(15)	114.6(1)	Ni–P(2)–C(16)	119.0(1)
Ni–S–C(18)	96.6(1)	Ni–O–C(17)	118.3(1)

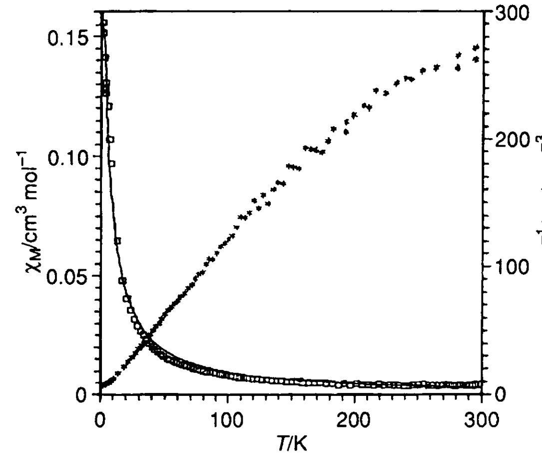

Fig. 3 Plot of the temperature dependence of the molar susceptibility χ_m (□) and $1/\chi_m$ (*) for $[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$. The solid line represents the best calculated values

and 1.37 μ_B at 1.5 K. Such a decrease may have several origins. Antiferromagnetic coupling and dipolar interaction between the nickel ions can align their moments antiparallel, causing a decrease in effective moment. Alternatively, single-ion anisotropy with the non-magnetic single state lowest, *e.g.* zero-field splitting, can lead to the same effects, as the fraction of nickel ions in the excited magnetic states decreases with temperature. Of course, both effects can occur in the same compound.

The slow decrease of the magnetic moment may result from antiferromagnetic exchange and/or dipolar interaction between the nickel(II) ions, whereas the rapid decrease at very low temperature may be caused by single-ion anisotropy of the high-spin nickel ion with $S = 1$. Although in the molecule of $[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$ there is only one paramagnetic nickel(II) ion located in an elongated-octahedral environment, whereas the other two nickel ions are in a square-planar environment which is diamagnetic, an antiferromagnetic exchange may still be transmitted by intermolecular dipolar interaction and by hydrogen bonding. Therefore we analysed the susceptibility data in terms of a model of single-ion zero-field splitting and at the same time took into account the intermolecular exchange interaction in a molecular field approach. The susceptibility can be expressed in the form of equation (1) with $x = D/kT$.[20–22] The data set for

$$\chi_m = \frac{2Ng^2\beta^2}{3k(T - \theta)} \frac{2x^{-1} - 2e^{-x}x^{-1} + e^{-1}}{1 + 2e^{-x}} \qquad (1)$$

compound **1** was fit by this equation, allowing D, g and θ to vary. The best parameters from the least-squares calculation were found to be $D = 3.76$ K, $g = 2.03$ and $\theta = -3.34$ K. The deviation factor $R\,[= \Sigma(\chi_m{}^{obs} - \chi_m{}^{calc})^2/\Sigma(\chi_m{}^{obs})^2]$ is 2.2×10^{-3}. A positive value of the parameter D means that the $m_s = 0$ state which lies below the $m_s = \pm 1$ state is the ground state.

Conclusion

Under given different reaction conditions, three different nickel(II) complexes of 2-sulfanylphenol with phosphine participation, *i.e.* $[Ni_3(OC_6H_4S)_2(HOC_6H_4S)_2(PBu^n{}_3)_2]\cdot 2EtOH$ **1**, $[Ni(OC_6H_4S)(PMe_2Ph)_2]$ **2** and $[NEt_3H][Ni(OC_6H_4S)(HOC_6H_4S)(PBu^n{}_3)]$ **3** were isolated. The bonding modes of the thiol in **1** are very different from that in the binuclear compound $[NEt_4]_2[Ni_2(OC_6H_4S)_2(HOC_6H_4S)_2]$ with no phosphine participation, where the nickel atoms in square-planar environment are chelated or bridged by $OC_6H_4S^{2-}$ and $HOC_6H_4S^-$ ligands in O_tS_t **IV** and HOS_b **II** fashions, respectively. Obviously, the presence of a phosphine favours the formation of the trinuclear system and the phosphine participation can modify the bonding modes of 2-sulfanylphenol. Although a number of trinuclear nickel(II) complexes of thiolates exhibiting various structural characteristics have been synthesized and characterized by single-crystal X-ray diffraction, to date only one cyclic trinuclear nickel(II) complex[5] with mixed phosphine and thiolate ligands has been isolated and characterized crystallographically. Complex **1** seems to be the first example of a quasi-linear trinuclear nickel(II) thiolate with phosphine participation, in which the Ni(1) centre displays an elongated octahedral geometry and the S atoms occupy the axial sites with an unusually long Ni–S bond [2.422(1) Å], while for other nickel(II) complexes containing thiolates or mixed thiolates and phosphines the metal atoms in most cases are four-co-ordinated with square-planar or tetrahedral geometry[17] except for the five-co-ordinated nickel(II) centre in cyclic trinuclear $[Ni_3(hcndt)_3(PPh_3)_3]$[5] which exhibits a distorted square-pyramidal geometry.

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