Polyhedron Vol. 6, No. 5, pp. 863–870, 1987
Printed in Great Britain

0277–5387/87 \$3.00+.00

THE SYNTHESIS, STRUCTURE AND SPECTROSCOPIC PROPERTIES OF THE DI- AND TRI-NUCLEAR Ni(II) THIOLATE COMPLEXES

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(*Received* 15 *May* 1986; *accepted* 4 *August* 1986)

Abstract—The anions $[Ni_2(edt)_3]^{2-}$ (edt = ethane-1,2-dithiolate) and $[Ni_3(edt)_4]^{2-}$ have been prepared by the reaction of $Na_2(edt)$ with $NiCl_2 \cdot 6H_2O$ and, with subsequent work-up, isolated as their $[PPh_4]^+$ salts. For the first time, the structure of di- and tri-nuclear Ni(II) thiolates with identical ligands can be compared. The complex $[PPh_4]_2[Ni_2(edt)_3]$ (**1**) crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters (at -152°C) $a = 12.861(7)$, $b = 21.057(14)$, $c = 10.324(5)$ Å, $\alpha = 96.03(3)°$, $\beta = 109.88(3)°$, $\gamma = 76.82(3)°$, and $Z = 2$, while $[PPh_4]_2[Ni_3(edt)_4]$ (**2**) crystallizes in the monoclinic space group $P2_1/c$ with (at -60°C) $a = 13.713(3)$, $b = 13.255(3)$, $c = 15.754(5)$ Å, $\beta = 96.53(2)°$ and $Z = 2$. The structures were solved by direct methods and Fourier techniques from 4576 and 2671 diffractometer data, respectively, and refined to respective R values of 0.0552 and 0.0649. In the anion of **1**, one of the ligands provides two terminal thiolate-groups, and the other two each provide one terminal and one μ-thiolate-group such that each Ni(II) has an approximately square planar coordination geometry. The central NiS_2Ni unit is not planar, being folded along the vector joining the two bridging sulphur atoms. The anion of **2** is best considered as chelation of two identical $[Ni(edt)_2]^{2-}$ units to a third, central Ni(II) atom. The anion has a crystallographically observed centre of symmetry, with the central nickel atom thus lying in a perfect plane formed by its four coordinated sulphur atoms. The outer two nickel atoms are approximately square planar and the $Ni(NiS_4)_2$ core exists in a chair conformation. Both of the anions described have short $Ni \cdots Ni$ distances [2.9414(22) in (**1**) and 2.8301(13) Å in (**2**)]. The structures and the spectroscopic properties achieved for these complexes are described and discussed herein.

Our interest in the thiolate chemistry of nickel was stimulated by reports that in several reduced and oxidized hydrogenases the primary coordination sphere of nickel contains several sulphur atoms[1,2] and by the paucity of well-characterized compounds of this type in the literature which might be considered useful structural analogues. Although nickel is found in its +3 oxidation level in the resting state of the hydrogenases,[1,2] the +2 level is involved in the catalytic cycle. Hence the synthesis and characterization of some nickel(II) thiolates was considered to be of importance as a necessary first step in a modelling approach.

Prior to this work being undertaken, a few structurally characterized homoleptic nickel(II) thiolates had been reported[3–9] but none with edt. In our investigation of this area the bidentate ligand ethane-1,2-dithiolate was employed because this ligand has recently found much utility in the thiolate chemistry of the first row transition metals[10,11,13–16] and has been shown to stabilize some of these metals in what is regarded as high oxidation levels.[11,13,16]

Herein, we report the preparation, spectroscopic, and structural characterization of the two title complexes, $[PPh_4]_2[Ni_2(edt)_3]$ and $[PPh_4]_2[Ni_3(edt)_4]$, which contribute to the structural diversity already established for existing nickel thiolates[3–9,12] and allow for the first time direct structural comparison

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of di- and tri-nuclear Ni(II) thiolates with identical ligands.

EXPERIMENTAL

All manipulations were performed using standard inert-atmosphere techniques. Acetonitrile was distilled from CaH_2 under a dinitrogen atmosphere and ethanol was dried over molecular sieves and degassed before use. Ethane-1,2-dithiol was used as received.

Proton NMR spectra were measured for concentrated solutions in $(CD_3)_2SO$ at 300 and 360 MHz on Varian XL-300 and Nicolet NT-360 instruments. Electronic spectra were obtained in CH_3CN or DMF solution on a 8450A Hewlett Packard UV–Vis spectrophotometer interfaced with a Hewlett Packard 7470A Plotter. IR spectra were recorded, with Nujol mulls between CsI plates, in the range 4000–200 cm^{-1} on a Perkin–Elmer 283 spectrometer. Electrochemical measurements were performed in the cyclic voltammetric mode with an IBM model EEC 25 voltammetric analyser in conjunction with a glassy carbon working electrode, a platinum-wire auxiliary electrode, and an SCE reference electrode. The supporting electrolyte was 0.1 M tetra-*n*-butylammonium perchlorate (TBAP), and concentrations of electroactive species were in the *c*. 5 mM range. Measurements were performed in MeCN solution, and potentials are quoted vs the normal hydrogen electrode (NHE) with ferrocene as an internal standard ($E_{1/2}$ = 0.400 V vs NHE).

Preparation of $[PPh_4]_2[Ni_2(SCH_2CH_2S)_3]$

Sodium metal (0.77 g, 34.0 mmol) was dissolved in EtOH (60 cm^3) and ethane-1,2-dithiol (1.40 cm^3, 17 mmol) added followed by solid $NiCl_2 \cdot 6H_2O$ (2.0 g, 8.4 mmol). Stirring at room temperature resulted in the formation of a white precipitate (NaCl) in a dark green solution within 0.5 h. The solution was filtered into a Schlenk tube containing PPh_4Br (7.4 g, 18 mmol). Intensely green coloured microcrystals of the product began precipitating almost immediately and after storage at room temperature for 24 h this product was collected by filtration, washed with two portions of an $EtOH/Et_2O$ mixture (10 cm^3, 1 : 1 composition) and dried *in vacuo*. The crude yield obtained was 2.8 g (52% with respect to nickel). After several days a further 0.55 g of product was isolated from the filtrate as very large chunky crystals which are intensely green coloured. The crude material is analytically and spectroscopically pure and crystals of a suitable size and quality for X-ray diffraction can be obtained from a slightly more dilute solution. Found: C, 60.7; H, 4.6; S, 18.5. $C_{54}H_{52}Ni_2P_2S_6$ requires C, 60.4; H, 4.9; S, 17.9%.

The crude product can be recrystallized by extracting with hot MeCN followed by slow cooling to room temperature, though this significantly reduces the overall yield (32%).

Employing a Ni : edt^{2-} ratio of 2 : 3 and following the procedure described above leads to the isolation of the same product in lower yield (1.7 g, 32%, crude product). Recrystallization from hot MeCN affords rhomb-shaped crystals which appear red-brown to transmitted light. [Found: C, 59.9; H. 5.0; S, 18.7%.) [Note: Although crystals of $[PPh_4]_2[Ni_2(edt)_3]$ obtained from reactions employing 2 : 1 and 3 : 2 ligand to metal ratios consistently lead to crystals which have different colours, their fully refined X-ray crystal structures are identical.

Preparation of $[PPh_4]_2[Ni_3(SCH_2CH_2S)_4]$

Sodium metal (0.58 g, 25 mmol) was dissolved in EtOH (60 cm^3) and ethane-1,2-dithiol (1.06 cm^3, 12.6 mmol) added followed by solid $NiCl_2 \cdot 6H_2O$ (1.50 g, 6.3 mmol). After *c*. 0.5 h the white precipitate (NaCl) was separated by filtration and PPh_4Br (5.55 g, 13.0 mmol) was added to the dark green filtrate to incipient crystallisation. The Schlenk tube was allowed to stand at room temperature for 36 h before the product was collected by filtration. The product was washed with two portions of an $EtOH/Et_2O$ mixture (8 cm^3, 1 : 1 composition) and dried *in vacuo*. The identity of this product was established as $[PPh_4]_2[Ni_2(edt)_3]$ (1.0 g, 29.6% yield). The filtrate from this product was then exposed to the atmosphere for 24 h by removing the septum cap and leaving the flask undisturbed. A mixture of black crystalline material and white solid was precipitated from solution. Anaerobic conditions were re-established and the mixture was collected by filtration and then extracted with either hot EtOH or hot MeCN. Brown crystals were obtained from the EtOH solution upon standing at room temperature for one week and from the MeCN solution upon storage in a freezer (*c*. −20°C) for three weeks. Crystals from the latter recrystallization were of a suitable quality for X-ray diffraction studies. The non-optimized yield of recrystallized material was 0.3 g (12% with respect to nickel). Found: C, 54.4; H, 4.7; S, 21.6. $C_{65}H_{56}Ni_3P_2S_8$ requires C, 55.0; H, 4.6; S, 21.0%.

Crystal structure determination

Crystal data are summarized in Table 1; details of the diffractometry, low-temperature facilities,

Table 1. Data for crystal structure analyses of $[PPh_4]_2[Ni_2(SCH_2CH_2S)_3]$ (**1**) and $[PPh_4]_2[Ni_3(SCH_2CH_2S)_4]$ (**2**)

	1	**2**
Molecular formula	$C_{54}H_{52}Ni_2P_2S_6$	$C_{56}H_{56}Ni_3P_2S_8$
M	1072.73	1131.44
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Temperature (°C)	-152	-60
a, Å	12.861(7)[a]	13.713(3)[b]
b, Å	21.057(14)	13.255(3)
c, Å	10.324(5)	15.754(5)
α, deg	96.03(3)	
β, deg	109.88(3)	96.53(2)
γ, deg	76.82(3)	
Z	2	2
U, Å^3	2558.75	2844.95
D_c, g cm^{-3}	1.392	1.321
Radiation	Mo–K_α(0.71069 Å)	Mo-K_α(0.71069 Å)
μ, cm^{-1}	10.711	12.871
Method	θ–2θ	θ–2θ
Crystal size, mm	$0.28 \times 0.24 \times 0.20$	$0.20 \times 0.30 \times 0.34$
Scan speed, deg min^{-1}	4.0	4.0
Scan width, deg	1.8 + dispersion	2.0 + dispersion
Scan range, deg	$6 \leqslant 2\theta \leqslant 45$	$6 \leqslant 2\theta \leqslant 45$
No. of reflections collected	6988	4360
No. of unique intensities	6714	3734
No. of observed intensities	4576	2671
Criterion for observed, $n[I \geqslant n\sigma(I)]$	3	3
Solution method	Direct	Direct
Final R	0.0552	0.0649
Final R_w	0.0537	0.0594
Goodness of fit	0.820	1.075

[a] 40 reflections at −152°C.

[b] 30 reflections at −60°C.

and computational procedures employed by the Molecular Structure Center are available elsewhere.[17] For **1** a systematic search of a limited hemisphere of reciprocal space yielded a set of reflections which exhibited no symmetry or extinctions. The choice of the centrosymmetric space group $P\bar{1}$ was confirmed by the subsequent solution and refinement of the structure. For **2** a similar search located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to space group $P2_1/n$. The structures were solved by a combination of direct methods and Fourier techniques and refined by full-matrix least-squares.

All non-hydrogen atoms of $[PPh_4]_2[Ni_2(edt)_3]$ (**1**) were readily located and the hydrogen atoms were located after initial refinement. However, there is a slight disorder problem in the anion at atoms C(12) and C(13). During refinement the hydrogen atoms moved to positions which gave unreasonable distances. A check of the root mean square displacements of the anisotropic atoms showed that the ellipsoids for C(12) and C(13) were quite elongated (.16.24.39) compared to the rest of the atoms. In the subsequent cycles of refinement the C(12) and C(13) atoms were kept isotropic and the hydrogen atoms associated with them were fixed. The structure refinement was completed using full-matrix least-squares with anisotropic thermal parameters on all non-hydrogen atoms (except C(12) and C(13)) and all hydrogen atoms were refined with isotropic thermal parameters (except H(9) to H(12)). The final difference map was essentially featureless except for a few peaks of *c*. 1e Å^{-3} in the vicinity of C(12) and C(13).

In the refinement of $[PPh_4]_2[Ni_3(edt)_4]$, non-hydrogen atoms were assigned anisotropic thermal parameters whilst hydrogens were allowed to vary isotropically. A final difference Fourier was essentially featureless, with the largest peak being 0.50 e Å^{-3}.

Final values of atomic positional and thermal coefficients and lists of F_o/F_c values have been deposited as Supplementary data with the Editor, from whom copies are available on request. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The structure of the anions of $[PPh_4]_2[Ni_2(edt)_3]$ (**1**) and $[PPh_4]_2[Ni_3(edt)_4]$ (**2**) are shown in Figs 1 and 2, respectively. In the anion of **1**, one of the ligands provides two terminal thiolate groups, and the other two each provide one terminal and one μ-thiolate group such that each Ni(II) has an approximately square planar coordination geometry. The central NiS_2Ni unit is not planar, being folded along the vector joining the two bridging sulphur atoms. The anion of **2** is best considered as chelation of two identical $[Ni(edt)_2]^{2-}$ units to a third, central Ni(II) atom. The anion has a crystallographically observed centre of symmetry, with the central nickel atom thus lying in a perfect plane formed by its four coordinated sulphur atoms.

In order to describe the detailed structure of these anions a consideration of the Ni—S bond lengths given in Table 2 is necessary. It can be seen that a simple classification of these bond lengths into 'terminal' and 'bridging' is not entirely adequate. Those Ni—S bonds which form part of a Ni—S—C—C—S—Ni five-membered chelate ring are, on average, significantly shorter than those Ni—S bonds which are not within this chelate, and yet the former group contains ostensibly bridging *and* terminal ligation. Therefore, the $[Ni_2(edt)_3]^{2-}$ anion may best be thought of as arising from the chelation of a $[Ni(edt)_2]^{2-}$ monomeric unit to a Ni(edt) fragment with a folding of the two square planes thus formed along the common S···S edge. Similarly, $[Ni_3(edt)_4]^{2-}$ may be viewed as the chelation of a central Ni(II) atom by two $[Ni(edt)_2]^{2-}$ units in such a way as to generate a chair-like configuration of the Ni_3S_8 core. This Ni_3S_8 fragment closely conforms to C_{2h} symmetry, there being a mirror plane passing through the three nickel atoms and the mid-points of the sulphur atoms and a C_2 axis perpendicular to this. Inclusion of the methylene groups in the anion lowers the symmetry from C_{2h} to the crystallographically observed C_i-1. There are precedents for the kind of description given above, viz., the trimeric complexes $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$[4] and $[Ni(Ni(NH_2CH_2CH_2S)_2)_2]^{2+}$.[5] The former comprises the chelation of a central $[Ni(S_2\text{-}o\text{-xyl})_2]^{2-}$ unit to two $Ni(S_2\text{-}o\text{-xyl})$ fragments whilst the latter is analogous to $[Ni_3(edt)_4]^{2-}$.

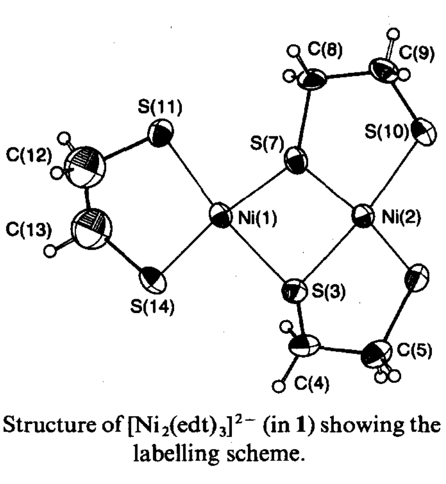

Fig. 1. Structure of $[Ni_2(edt)_3]^{2-}$ (in **1**) showing the atom-labelling scheme.

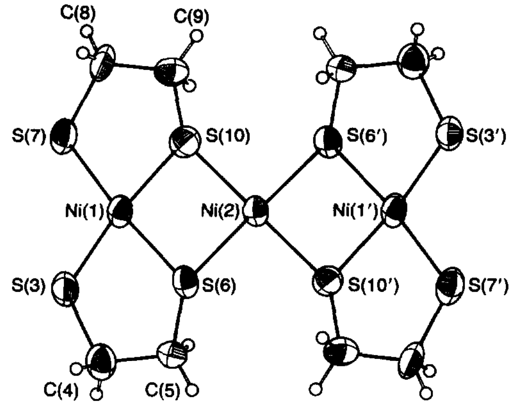

Fig. 2. Structure of $[Ni_3(edt)_4]^{2-}$ (in **2**) showing the atom-labelling scheme.

Grouping the Ni—S bonds in the manner described above, i.e. within and without a chelate ring, gives the following average distances: $[Ni_2(edt)_3]^{2-}$, 2.181(14) and 2.216(13) Å; $[Ni_3(edt)_4]^{2-}$, 2.183(8) and 2.217(9) Å; $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$,[4] 2.192(10) and 2.226(5) Å; $[Ni(Ni(NH_2CH_2CH_2S)_2)_2]^{2+}$,[5] 2.155(1) and 2.212 Å. With the exception of the two Ni—S bond distances within the Ni—S—C—C—N—Ni chelate ring of the latter being slightly shorter than the corresponding distances in the edt and S_2-*o*-xyl complexes, there are no significant differences between the four complexes with respect to their Ni—S bond lengths. The Ni—S bond lengths in the $[Ni_2(SEt)_6]^{2-}$ anion are comparable to those lying outside a chelate ring in the four complexes above [$Ni—S_b$ = 2.220(6), $Ni—S_t$ = 2.208(8) Å].[12]

There are several notable differences between the $[Ni_2(edt)_3]^{2-}$ and $[Ni_2(SEt)_6]^{2-}$[12] anions.

Table 2. Selected interatomic distances (Å) and angles (deg) for the anions in $[PPh_4]_2[Ni_2(S_2C_2H_4)_3]$ (**1**) and $[PPh_4]_2[Ni_3(S_2C_2H_4)_4]$ (**2**)

$[Ni_2(edt)_3]^{2-}$ (**1**)		$[Ni_3(edt)_4]^{2-}$ (**2**)	
		Ni—S_t	
Ni(2)—S(6)	2.2032(25)	Ni(1)—S(3)	2.189(3)
Ni(2)—S(10)	2.1894(24)	Ni(1)—S(7)	2.1893(28)
Ni(1)—S(11)	2.1680(25)		
Ni(1)—S(14)	2.1774(25)		
		Ni—S_b	
Ni(2)—S(3)	2.1673(24)	Ni(1)—S(6)	2.1773(26)
Ni(2)—S(7)	2.1778(25)	Ni(1)—S(10)	2.175(3)
Ni(1)—S(7)	2.2250(25)	Ni(2)—S(6)	2.2232(23)
Ni(1)—S(3)	2.2071(24)	Ni(2)—S(10)	2.2102(26)
		Ni···Ni	
Ni(1)···Ni(2)	2.9414(22)	Ni(1)···Ni(2)	2.8301(13)
		S···S	
S(3)···S(7)	2.820(3)	S(6)···S(10)	2.862(3)
		S_b—Ni—S_b	
S(3)—Ni(1)—S(7)	79.01(9)	S(6)—Ni(1)—S(10)	82.23(10)
S(3)—Ni(2)—S(7)	80.92(9)	S(6)—Ni(2)—S(10)	99.59(9)
		S(6)—Ni(2)—S(10′)	80.41
		S_t—Ni—S_t	
S(11)—Ni(1)—S(14)	92.19(10)[a]	S(3)—Ni(1)—S(7)	91.29(11)
S(6)—Ni(2)—S(10)	93.74(10)		
		Ni—S_b—Ni	
Ni(1)—S(7)—Ni(2)	83.83(9)	Ni(1)—S(6)—Ni(2)	80.04(8)
Ni(1)—S(3)—Ni(2)	84.50(8)	Ni(1)—S(10)—Ni(2)	80.38(9)
		S_b—Ni—S_t	
S(7)—Ni(1)—S(11)	93.83(10)	S(3)—Ni(1)—S(6)	93.10(10)
S(3)—Ni(1)—S(14)	95.28(10)	S(7)—Ni(1)—S(10)	93.02(11)

[a] This is the only S—Ni—S angle that occurs *inside* a chelate ring in either (**1**) or (**2**).

$[Ni_2(SEt)_6]^{2-}$ is centrosymmetric and is formed by edge sharing of two planar units to generate an Ni_2S_2 *planar* rhomb.[12] In $[Ni_2(edt)_3]^{2-}$ there is no centre of symmetry and the Ni(1,2)S(3,7) core is not planar, there being a folding along the S(3)···S(7) vector. There is a dihedral angle of 119.07° at the intersection of the two NiS_4 planes. This has the effect of bringing the two Ni atoms closer together than in $[Ni_2(SEt)_6]^{2-}$ [2.9414(22) vs 3.355(2) Å] and to make the Ni—S—Ni bond angle in the bridge more acute [83.83(9) and 84.50(8) ° vs 98.2(1)°]. In $[Ni_2(edt)_3]^{2-}$, Ni(1) lies in the least squares plane formed by S(3,7,11,14) (maximum deviation, S(7) 0.085 Å) and Ni(2) is perpendicularly displaced by −0.08 Å from the least squares plane S(3,6,7,10) (maximum deviation, S(3,7) 0.048 Å).

The central nickel atom Ni(2) and the four attached sulphur atoms are required by the crystallographic centre of symmetry, located at Ni(2), to be exactly planar in $[Ni_3(edt)_4]^{2-}$. There is a deviation, though, from perfect square planarity of these sulphur atoms as evidenced by the S(6)—Ni(2)—S(10) angle of 99.59(9)°. Each of the two outer nickel atoms is perpendicularly displaced from its S(3,6,7,10) and S(3′,6′,7′,10′) least squares plane by 0.0874 Å in the direction opposite to the side of the central nickel atom Ni(2). In $Ni(Ni(NH_2CH_2CH_2S)_2)_2^{2+}$ the two outer nickel atoms are similarly displaced, by 0.12 Å.[5] Ni(2) is 1.556 Å from the least squares plane formed by S(3,6,7,10) (maximum deviation by S(10), 0.00979 Å).

In order to try and rationalize the degree of folding along the S···S vector and the Ni···Ni distances observed in this and other, similar complexes, Table 3 was compiled. This gives a selec-

Table 3. Comparison of selected distances (Å) and angles (deg) in some thiolate-bridged complexes of nickel(II)

	Ni···Ni	Ni—S—Ni	S···S	Dihedral[18] angle	Ref.
$[Ni_2(SEt)_6]^{2-}$	3.355(2)	98.2(1)	2.906(4)	180	12
$[Ni_3(SEt)_8]^{2-}$	3.04	87		< 180	12
$[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$	3.016(1) 3.131(1)	85.66(7)– 90.26(7)	2.735(2) 2.687(2)	< 180	4
$[Ni_2(edt)_3]^{2-}$	2.9414(22)	83.83(9) 84.50(8)	2.820(3)	119.07	[a]
$[Ni_3(edt)_4]^{2-}$	2.8301(13)	80.04(8) 80.38(9)	2.862(3)	113.19	[a]
$[Ni_2(SBz)_2(Bzttc)_2]$[b]	2.795(3)	79.5	2.826(5)	114.3	19
$[Ni_2(SEt)_2(Etttc)_2]$[c]	2.763	78.4	*c*. 2.84[d]	110.2	20
$Ni(Ni(NH_2CH_2CH_2S)_2)_2^{2+}$	2.733(7)	77.5	2.89(1)	109	5

[a] This work.

[b] SBz = $SCH_2C_6H_5$; Bzttc = $S_2CSCH_2C_6H_5$.

[c] Etttc = $S_2CSC_2H_5$.

[d] Distance approximated.

tion of distances and bond angles in some thiolate-bridged nickel complexes. The most notable feature is a variation in Ni···Ni distances of more than 0.6 Å. There appear to be a number of factors which might be responsible for the specific metal–metal distances found. These include, (i) direct, net positive, Ni···Ni interaction, (ii) the stereochemistry at the bridging sulphur atom (any chelate constraints will be manifested in this), (iii) the total charge provided by the ligand set, (iv) the S···S separation of the bridging sulphur atoms, and (v) ligand–ligand steric interactions. Crystal packing may or may not be an important additional factor. It is quite clear that no one factor dominates over all of the others and it would appear that they are capable of assuming different relative importances.

The nickel–nickel separation in $[Ni_2(edt)_3]^{2-}$ and $[Ni_3(edt)_4]^{2-}$ is certainly short enough to permit some kind of a net weak positive interaction, though its nature is not clear. Dahl has proposed that this is due to overlap of the filled $3d_z{}^2$ orbitals on Ni.[5] Similarly, the bridging S···S separation is *c* 0.4 Å shorter than would be expected for a non-bonding interaction, but there is nothing to suggest that it is optimal in these two complexes. Chelate constraints alone cannot be responsible for the resulting Ni···Ni distances, because a difference of 0.6 Å exists between the two dimers[12,20] which both have unconstrained $C_2H_5S^-$ as bridging ligands.

From a consideration of the two trimeric complexes $[Ni_3(edt)_4]^{2-}$ and $Ni(Ni(NH_2CH_2CH_2S)_2)_2^{2+}$ we can make some interesting observations. The similarities between them indicate that of those factors (i)–(v) listed, (iii) should be the one most responsible for the difference in observed Ni···Ni distance. As noted earlier in this section, the Ni—S bonds found within the Ni—S—C—C—N—Ni chelate rings are the shortest (2.155 Å) Ni—SR bonds of any in the complexes under discussion. A reason for this might be that the aminoethanethiolate effectively provides two neutral and two negatively charged ligands for the outer nickel atoms, whereas the edt provides four negatively charged ligands. This results in a larger net positive charge in the nickel in the former which consequently leads to shorter Ni—S distances. As a result, the Ni···Ni separation is decreased. Indeed, of the compounds listed in Table 3, $Ni(Ni(NH_2CH_2CH_2S)_2)_2^{2+}$ has the shortest Ni···Ni distance and is the only one to have a neutral donor atom in its nickel coordination sphere. Pursuing this idea a little further, it could be argued that the trithiocarbonate ligands in $[Ni(CS_3C_2H_5)(SC_2H_5)]_2$[20] and $[Ni(CS_3CH_2Ph)(SCH_2Ph)]_2$[19] have only a uninegative charge which allows the Ni—S bonds in the bridge to shorten (to 2.186 and 2.189 Å) with respect to those average distances found in the compounds having purely thiolate coordination. This then leads to the shorter Ni···Ni distances found in these two complexes. Having said this, however, the effect of total charge provided by the ligand set cannot explain the difference in Ni···Ni separation observed for the $[Ni_2(edt)_3]^{2-}$ and $[Ni_3(edt)_4]^{2-}$ anions. In these two anions, the mean of four Ni—S_b bond distances are identical. The shorter Ni···Ni separation in the trimer is a net result of more acute Ni—S—Ni and dihedral angles and larger S···S separation. All three changes are consistent with a shortening of the Ni···Ni separation, given no variation in Ni—S_b lengths, but it is impossible to categorize them as cause or consequence.

The data in Table 3 do show that, without exception, a shortening of the Ni···Ni distance results in a more acute Ni—S—Ni angles in the bridge and a more acute dihedral angle. The S—Ni—S bond angles within the bridging unit tend to lie in the range 79–84° for the complexes listed in Table 5. Exceptions to this are one of the angles in the $[Ni_3(edt)_4]^{2-}$ anion which is exceptionally large (99.59(9)°) and the angle in $[Ni_2(SB_z)_2(S_2CSCH_2C_6H_5)_2]$ (98.3°).[19] [The data provided[4] for the $[Ni_3(S_2\text{-}o\text{-xyl})_4]^{2-}$ anion do not permit a definitive comparison.]

¹H NMR, IR, UV–VIS AND ELECTROCHEMICAL STUDIES

¹H NMR spectroscopy proved to be a very effective analytical tool in this work. Integration of the ligand methylene protons vs those of the PPh_4^+ cation accurately determines the ligand to cation ratio. Also, the spectrum of $[PPh_4]_2[Ni_3(edt)_4]$ is quite distinctly different from and more complex than, that of $[PPh_4]_2[Ni_2(edt)_3]$ in the methylene proton chemical shift region. In the $[Ni_2(edt)_3]^{2-}$ anion, the proton resonances appear as two multiplets having an approximate relative intensity of 1 : 5 centred at 1.72 and 1.95 ppm respectively. The room temperature spectrum of the $[Ni_3(edt)_4]^{2-}$ complex appears to be much more complicated than one would expect from the solid state structure. The methylene proton resonances are found between 1.65 and 2.70 ppm. Within this region there are two reasonably well-resolved multiplets each having six lines centered at 1.7 and 2.65 ppm; the remaining features are relatively broad. It is conceivable that fluxional processes are in effect in the DMSO solvent; this might involve breaking the weaker Ni—S bonds or the existence of different isomers in solution. For both compounds the PPh_4^+ proton resonances are centered around 8.0 ppm as expected.

On the basis of their IR spectra, recorded between 4000 and 200 cm^{-1}, compounds **1** and **2** are essentially indistinguishable.

The UV–Vis spectra were recorded for **1** and **2** on solutions prepared and maintained under an inert atmosphere. **1** dissolves to give a green coloured solution in MeCN and **2** gives a red/brown coloured solution in MeCN and in DMF. Within *c.* 2 h a solution of **2** in MeCN will turn cloudy. The spectrum of **1** has $\lambda_{max}(\varepsilon_m)$ at 468 nm (3,459) and 624 nm (954) which agree reasonably well with the data reported previously for this complex anion.[10] The spectrum of **2** was recorded for both MeCN and DMF solutions and λ_{max} were found at 297(sh) nm (15,561), 325(sh) (13,225), 424 (3818) and 538 (2806) in MeCN and at 432 nm (6775), 542 (4944), and 720 (1576) in DMF. These spectra show a slight shift in band position in CH_3CN vs DMF and both clearly differ from the values reported[10] for putative $[NEt_4]_2[Ni_3(edt)_4]$ in CH_3CN [392 nm (2200) and 468 (1280)]. Unfortunately, neither **1** nor **2** displayed electrochemically reversible behaviour when studied by cyclic voltammetry. **1** gave three oxidation peaks, at $E_{p,a} = -0.32$, -0.03 and $+0.73$ V vs NHE and **2** gave two oxidation peaks, at $E_{p,a} = -0.06$ and $+0.73$ V.

In conclusion, use of the edt^{2-} ligand has allowed nickel(II) thiolate complexes of differing nuclearity to be prepared. Structural characteristics of di- and tri-nuclear products can be compared for the first time under identical ligation. Unfortunately, use of the edt^{2-} ligand does not result in easier accessibility of the nickel(III) oxidation level, as judged by our electrochemical results are least, a situation we had hoped might result given the stabilization by this ligand of manganese(III)[13,16] and cobalt(III).[11] However, the continuing desire for nickel(III) species with sulphur ligation to model the nickel(III) sites of hydrogenases demands further effort in this area, perhaps with mixed ligation around the metal center.

Acknowledgements—J.R.N. is a recipient of a U.K. SERC NATO Postdoctoral Fellowship. We thank the Bloomington Academic Computing Center for a gift of computer time.

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