Australian Journal
of Chemistry

A journal for the publication of original research
in all branches of chemistry and chemical technology

www.publish.csiro.au/journals/ajc

X-Ray Study of Two Novel Nickel(II)–Thiosulfate Compounds

Eleonora Freire,[A] *Sergio Baggio,*[A] *Leopoldo Suescun*[B] *and Ricardo Baggio*[C,D]

[A] Universidad Nacional de la Patagonia, Sede Puerto Madryn, and
CenPat, CONICET, 9120 Puerto Madryn, Chubut, Argentina.
[B] Laboratorio de Cristalografía y Química del Estado Sólido, Facultad de Química,
Universidad de la República, Montevideo, Uruguay.
[C] Departamento de Física, Comisión Nacional de Energía Atómica,
Avda del Libertador 8250, 1429 Buenos Aires, Argentina.
[D] Author to whom correspondence should be addressed (e-mail:
baggio@cnea.gov.ar).

Two novel nickel thiosulfate complexes have been prepared and their crystal structures determined: $NiS_2O_3(dmph)(H_2O)\cdot H_2O\cdot CH_3OH$ (1) (dmph = 2,9-dimethyl-1,10-phenanthroline), which to our knowledge is the first pentacoordinated nickel thiosulfate complex described so far, and $NiS_2O_3(dmph)$ (2), a hexacoordinated complex which displays a thiosulfate binding mode with no precedents in the literature, viz. bridging solely through oxygen. Compound (1) is monoclinic, $C2/c$, a 26.269(5), b 7.641(3), c 18.381(3) Å, β 97.00(2)°, V 3662(2) Å^3, Z 8, conventional R (on F) being 0.049 for 2217 N_o observed reflections ($I > 2\sigma(I)$). Compound (2) is also monoclinic, $P2_1/n$, a 11.108(2), b 10.955(2), c 11.666(2) Å, β 103.32(3)°, V 1381.4(5) Å^3, Z 4, R 0.036, N_o 2497.

Keywords. Bridging thiosulfate; five-coordinate nickel.

Introduction

The thiosulfate ion has proved to be a very versatile ligand in transition-metal coordination compounds, with a geometry dependent on the type of coordination present.

Several studies on thiosulfate salts,[1] where the anion is ionic in nature, show it to present a symmetric C_{3v} geometry, with a narrow range of bond distances and angles (S–S 1.987–2.031 Å, S–O 1.465–1.493 Å). The situation is different in coordination compounds. This is clearly shown by a survey we made on the subset of structures where the anion is solely coordinated to transition metals. In this analysis we disregarded those mixed complexes, which also include alkali metal cations, which very often display quite cumbersome interaction schemes due to far reaching Coulombic interactions. Our search reveals that the ligand can act as monodentate, bidentate or bridge, conforming to seven different ways of coordination, with associated effects on the anion geometry. The results are summarized in Fig. 1, types *1–7*.[2–28] Analysis of the structures therein shows that one of the most significant effects which coordination can have on the geometry of thiosulfate is the lengthening of the S–S bond, with a concomitant shortening of the S–O bonds, in coordinations of type *1* and *2* (M = Co, Pd, Mo, Os, Sn, Ru, Fe, Zn, Cr, Pt). Shifts towards higher frequencies of the infrared S–O stretching modes[29] agree well with these crystallographic results. In the few structures corresponding to types *3–7*, in which sulfur and oxygen are both involved in coordination, a significant S–O bond lengthening occurs.

Pursuant to our long-term interest in novel coordination schemes in thiosulfato complexes we have been able to produce some (so far unique) examples of new coordination modes, viz. types *4*, *6* and *7* in Fig. 1. This was achieved
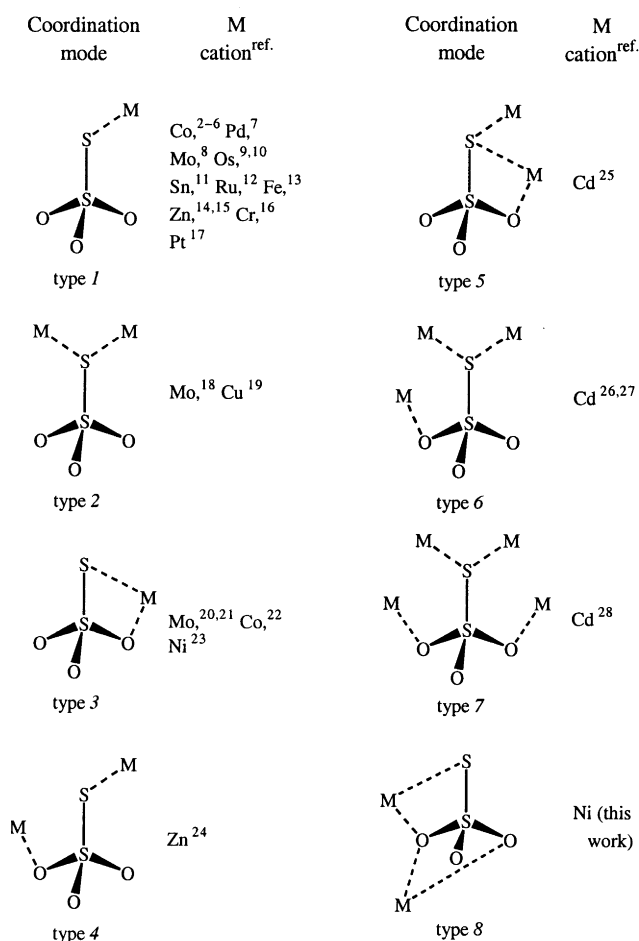

Fig. 1. Different coordination modes for transition-metal thiosulfate complexes.

through the simple policy of trying to generate thiosulfate complexes of cations which behave as borderline acids in the Pearson classification scale: in these cases, the metallic ions are expected to bind to thiosulfate both to the hard (O) as well as to the soft (S) end, thus resulting in a potential variety of coordination modes, depending on other concurring factors, viz. crystal field stabilization, shapes of accompanying ligands, intermolecular forces such as van der Waals and hydrogen bonding, etc.

As the latest outcome of this serial work, we report herein the crystal structures of two novel, quite different though rather similarly formulated, nickel(II) thiosulfates: $NiS_2O_3(dmph)(H_2O) \cdot H_2O \cdot CH_3OH$ (1) (dmph = 2,9-dimethyl-1,10-phenanthroline), which to our knowledge is the first pentacoordinated nickel thiosulfate complex described so far, and $NiS_2O_3(dmph)$ (2), a hexacoordinated complex which displays a thiosulfate binding mode with no precedents in the literature, viz. bridging solely through oxygen (Fig. 1, type *8*).

Experimental

Syntheses

Both compounds were obtained from diffusion of a mixture of aqueous solutions of nickel nitrate and sodium thiosulfate into a methanolic solution of dmph (2,9-dimethyl-1,10-phenanthroline). Two trials were made with different reactant concentrations. In the first one, with a 2 : 5 : 1 ratio, a few needles of (1) appeared at a certain stage of the process, the best of which were conveniently picked up. On standing, the crystallized material not removed from the solution was completely digested by the mother liquors to give rise to the growth of specimens of the seemingly more stable phase (2). In the second trial, with a 1 : 1 : 1 reactant ratio, only this latter phase (2) appeared, in the form of small, stable light-green plates.

Materials and Measurements

All starting materials were purchased from Aldrich and used without further purification. Elemental analyses (C, H, N) on compound (2) were performed on a Carlo Erba EA 1108 instrument. Nickel was determined on a Shimadzu AA6501 spectrophotometer. Compound (1) could not be analysed due to lack of material. Infrared spectra were recorded on a Nicolet 510 P Fourier-transform infrared spectrophotometer by using the KBr pellet technique. Thermogravimetric analyses were recorded on a Shimadzu DTG50 thermal analyser under an atmo-
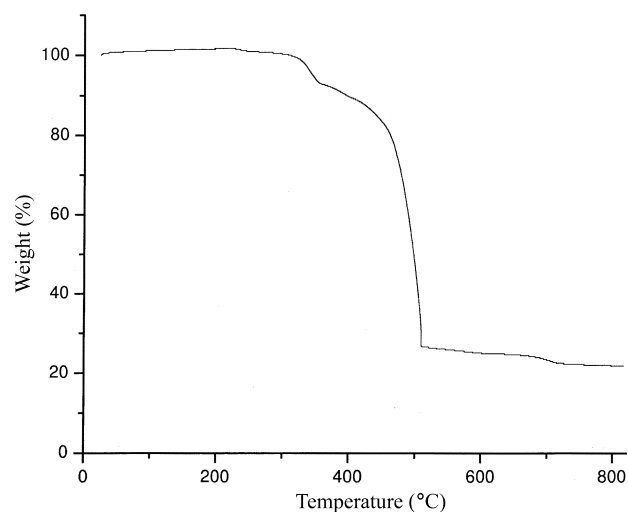
Fig. 2. Thermogram of (2).

Table 1. Non-hydrogen positional and isotropic displacement parameters

Structure	Atom	x	y	z	U_{eq} (Å²)
(i)	Ni	0.1342(1)	0.4590(1)	0.1165(1)	0.034(1)
	S(1)	0.0916(1)	0.2159(2)	0.0576(1)	0.050(1)
	S(2)	0.1074(1)	0.1252(2)	0.1601(1)	0.048(1)
	O(1)	0.1447(2)	-0.0147(5)	0.1624(3)	0.069(2)
	O(2)	0.1297(2)	0.2825(5)	0.1995(2)	0.054(1)
	O(3)	0.0611(2)	0.0727(6)	0.1893(3)	0.087(2)
	N(1)	0.1172(1)	0.6207(5)	0.0294(2)	0.039(1)
	N(2)	0.2042(1)	0.4629(5)	0.0813(2)	0.038(1)
	C(1)	0.0730(2)	0.7010(7)	0.0073(3)	0.049(1)
	C(2)	0.0653(2)	0.7801(8)	-0.0621(3)	0.064(2)
	C(3)	0.1018(3)	0.7741(8)	-0.1077(3)	0.065(2)
	C(4)	0.1489(2)	0.6924(7)	-0.0848(3)	0.049(1)
	C(5)	0.1904(3)	0.6836(8)	-0.1278(3)	0.064(2)
	C(6)	0.2353(3)	0.6091(8)	-0.1008(3)	0.061(2)
	C(7)	0.2425(2)	0.5332(7)	-0.0295(3)	0.049(1)
	C(8)	0.2885(2)	0.4571(7)	0.0030(3)	0.057(2)
	C(9)	0.2914(2)	0.3920(7)	0.0708(3)	0.055(1)
	C(10)	0.2487(2)	0.3941(6)	0.1102(3)	0.047(1)
	C(11)	0.2014(2)	0.5342(6)	0.0128(3)	0.038(1)
	C(12)	0.1548(2)	0.6169(6)	-0.0164(2)	0.040(1)
	C(13)	0.0334(2)	0.7029(8)	0.0595(3)	0.059(2)
	C(14)	0.2519(2)	0.3285(9)	0.1879(3)	0.069(2)
	O(1w)	0.1430(2)	0.6425(5)	0.1947(2)	0.050(1)
	O(2w)	0.0000	0.3340(10)	0.2500	0.098(2)
	O(1M)	0.0768(3)	0.5953(9)	0.2938(4)	0.095(2)
	C(1M)	0.0629(7)	0.7353(19)	0.3296(9)	0.183(6)
	O(2M)	0.0000	-0.145(3)	0.2500	0.095(2)
	C(2M)	-0.029(2)	-0.091(9)	0.188(2)	0.183(6)
(2)	Ni	0.9794(1)	0.0515(1)	0.6369(1)	0.021(1)
	S(1)	1.2016(1)	0.0454(1)	0.6996(1)	0.029(1)
	S(2)	1.1746(1)	-0.0929(1)	0.5837(1)	0.024(1)
	O(1)	1.2041(2)	-0.0547(2)	0.4710(2)	0.031(1)
	O(2)	1.0349(2)	-0.1070(2)	0.5532(2)	0.028(1)
	O(3)	1.2383(2)	-0.2023(2)	0.6315(2)	0.042(1)
	N(1)	0.9601(2)	0.2154(2)	0.7166(2)	0.023(1)
	N(2)	0.9164(2)	-0.0163(2)	0.7779(2)	0.022(1)
	C(1)	0.9865(2)	0.3277(2)	0.6873(2)	0.027(1)
	C(2)	0.9679(3)	0.4291(3)	0.7551(3)	0.036(1)
	C(3)	0.9233(3)	0.4150(3)	0.8528(3)	0.037(1)
	C(4)	0.8984(3)	0.2973(3)	0.8880(2)	0.030(1)
	C(5)	0.8547(3)	0.2723(3)	0.9929(3)	0.035(1)
	C(6)	0.8320(3)	0.1579(3)	1.0231(3)	0.034(1)
	C(7)	0.8488(2)	0.0561(3)	0.9508(2)	0.027(1)
	C(8)	0.8239(3)	-0.0644(3)	0.9769(3)	0.033(1)
	C(9)	0.8439(3)	-0.1562(3)	0.9051(2)	0.031(1)
	C(10)	0.8922(2)	-0.1307(2)	0.8056(2)	0.026(1)
	C(11)	0.8935(2)	0.0768(2)	0.8487(2)	0.023(1)
	C(12)	0.9176(2)	0.1989(2)	0.8165(2)	0.023(1)
	C(13)	1.0357(3)	0.3460(3)	0.5795(3)	0.038(1)
	C(14)	0.9185(3)	-0.2333(3)	0.7306(3)	0.034(1)

Table 2. Selected interatomic distances (Å)

Structure	Atoms	Distance	Atoms	Distance
(1)	Ni–O(1w)	2.000(4)	S(1)–S(2)	2.003(2)
	Ni–N(2)	2.023(4)	S(2)–O(3)	1.444(4)
	Ni–N(1)	2.030(4)	S(2)–O(1)	1.448(4)
	Ni–O(2)	2.049(3)	S(2)–O(2)	1.487(4)
	Ni–S(1)	2.362(2)		
(2)	Ni–N(1)	2.055(2)	Ni–S(1)	2.409(1)
	Ni–N(2)	2.068(2)	S(1)–S(2)	2.007(1)
	Ni–O(1)^A	2.135(2)	S(2)–O(3)	1.438(2)
	Ni–O(2)	2.151(2)	S(2)–O(1)	1.486(2)
	Ni–O(2)^A	2.270(2)	S(2)–O(2)	1.517(2)

^{A} $2-x, -y, 1-z$.

sphere of air at a heating rate of 5°C min^{-1}. Powder X-ray diffraction data were collected on a Phillips X'Pert diffractometer; monochromatic Cu Kα radiation was used.

Elemental Analysis, Infrared Spectrum and Thermogravimetric Analysis

The formulation of (2) was supported by elemental analysis, infrared spectroscopy and thermogravimetric analysis. The one for (1) was provided by the structure resolution. Single-crystal X-ray analyses were carried out for both complexes.

Data for (2) (Found: C, 37.9; H, 2.7; N, 6.4; Ni, 27.8; S, 14.5. $C_{14}H_{12}N_2$ NiO_3S_2 requires C, 37.9; H, 2.7; N, 6.3; Ni, 27.7; S, 14.5%). Infrared (KBr, cm^{-1}): 1593m, 1512m, 1501m, 1435m, 1416w, 1373m, 1360w, 1233vs ($\nu_{asym\,SO}$) ($S_2O_3^{2-}$), 1159m, 1150w, 1040vs ($\nu_{sym\,SO}$) ($S_2O_3^{2-}$), 1003w, 929s, 870s (dmph), 667vs, 557s. Fig. 2 shows the thermal behaviour. The compound remains fairly stable up to *c.* 320°C, where a slow degradation process starts, with an abrupt mass drop (74%) in the range 460–510°C. The final stage corresponds a slightly decreasing plateau which leads to a final weight loss of 79% at 800°C. The expected mass loss for complete combustion into NiO (identified by the X-ray powder diffraction pattern[30]) is 80.3%.

Structure Determination

Unique room temperature diffractometer data sets (θ/2θ scan mode, $2\theta_{max}$ 55°, monochromatic Mo Kα radiation, λ 0.7107 Å, *T* 295 K) were measured, yielding *N* independent reflections of which N_o were considered observed, with an internal consistency R_{int}. In all cases the structure resolution was achieved routinely by direct methods and difference-Fourier syntheses. The structures were refined by least squares on F^2, with anisotropic displacement parameters for the non-hydrogen atoms. Hydrogen atoms unambiguously defined by the stere-
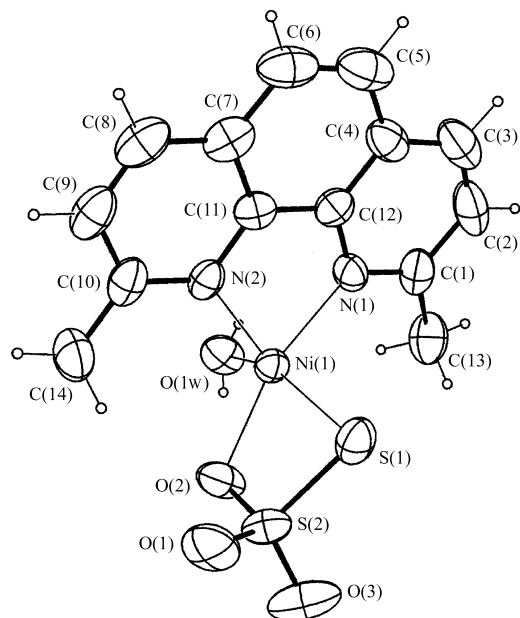
ochemistry (C–H) were placed at their calculated positions and allowed to ride on their host carbons both in coordinates as well as in thermal parameters; methyl hydrogens were further allowed to rotate around the C–C bond. Those attached to oxygens (O–H) were picked up from the late difference-Fourier synthesis and refined with free *U* values but restrained O–H and H–H distances. In this way, all hydrogens except those corresponding to the disordered methanol solvate in (1) were included in the models. All calculations to solve and refine the structures were carried out with the computer programs SHELXS97, SHELXL97, SHELXTL-PC and Parst.[31–34] Pertinent results are given in Tables 1 and 2, and Figs 3–6. Deposited material includes coordinates and thermal parameters for all atoms, and structure factor amplitudes (copies are available, until 31 December 2005, from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066).
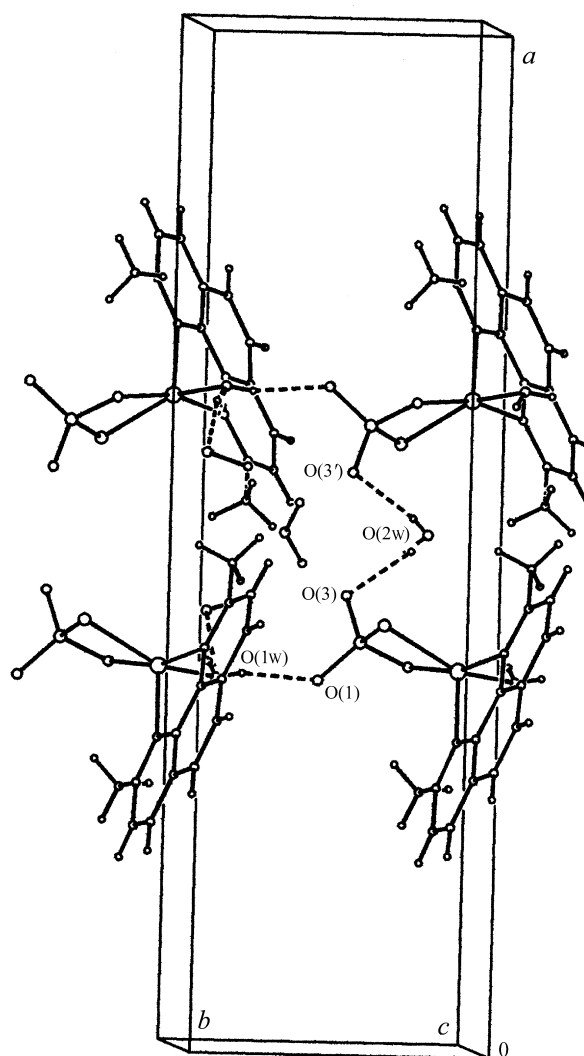

Fig. 3. Molecular drawing of monomer in (1) showing atom labelling. Thermal ellipsoids are drawn at 50% level.

Fig. 4. Packing diagram for (1) displaying the main hydrogen-bonding interactions.

Table 3. Hydrogen bonding in (1)

O_d	H_d	O_a	O_d–H_d (Å)	$H_d\cdots O_a$ (Å)	$O_d\cdots O_a$ (Å)	O_d–$H_d\cdots O_a$ (deg)
O(1w)	H(1wA)	O(1M_A)	0.72(6)	1.99(6)	2.69(1)	166(6)
O(2w)	H(2w)	O(3)	0.73(8)	2.16(6)	2.87(1)	164(6)
O(1w)	H(1wB)	O(1)[*x*, 1+*y*, *z*]	0.73(4)	1.98(4)	2.69(1)	164(4)

Crystal/Refinement Data

(1) $C_{15}H_{19}N_2NiO_{5.50}S_2$, M 438.15. Monoclinic, space group $C2/c$ (C_{2h}^6, No.15), a 26.269(5), b 7.641(3), c 18.381(3) Å, β 97.00(2)°, V 3662(2) Å^3. $D_c(Z=8)$ 1.59 g cm^{-3}; F_{000} 1816. Specimen 0.12 by 0.18 by 0.22 mm^3; μ 1.32 mm^{-1}, θ range 2.23–27.50°, $0 \leq h \leq 34$, $0 \leq k \leq 9$, $-23 \leq l \leq 23$, $N(R_{int})$ 4195(0.041), N_o 2217, R 0.049, wR 0.131, $\Delta(\rho)$ 0.7/–0.59 e Å^{-3}.

(2) $C_{14}H_{12}N_2NiO_3S_2$, M 379.09. Monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14), a 11.108(2), b 10.955(2), c 11.666(2) Å, β 103.32(3)°, V 1381.4(5) Å^3. $D_c(Z=4)$ 1.82 g cm^3, F_{000} 776. Specimen 0.15 by 0.15 by 0.20 mm^3; μ 1.72 mm^{-1}, θ range 2.28–27.48°, $0 \leq h \leq 14$, $0 \leq k \leq 14$, $-15 \leq l \leq 14$, $N(R_{int})$ 3175(0.056), N_o 2497, R 0.036, wR 0.097, $\Delta(\rho)$ 1.21/–0.47 e Å^{-3}.

Results and Discussion

Structure of $NiS_2O_3(dmph)(H_2O)\cdot H_2O\cdot CH_3OH$ (1)

Compound (1) is monomeric, with the Ni^{2+} cation surrounded by a pentacoordinated environment (Fig. 3), the first case to be reported in a nickel–thiosulfato complex. This coordination is achieved through the thiosulfate group acting as a bidentate ligand through S(1) and O(2), the bidentate dmph binding through both nitrogens, and, finally, one aqua ligand. The geometry of the coordination polyhedron is roughly that of a square pyramid, where N(2) from the dmph occupies the apical site and the rest define a rather distorted square base (largest deviation from the least-squares plane: 0.10(1) Å, for O(2); departure of Ni(1) from the plane: 0.34(1) Å towards the apical site; Ni(1)–N(2) line, 16° away from the normal to the plane).

As expected for this small coordination number, the three different types of bonds to nickel (Ni–S, Ni–O and Ni–N) are significantly shorter than those in octahedral complexes, in order to maintain the bond valence of the Ni^{2+} ion.

The monomers are linked through hydrogen bonding interactions mediated by the water molecules: the aqua one joins polyhedra together into chains in the <010> direction (O(1w)–H(1wB)···O(1)), while the hydration O(2w) joins pairs of chains into 'strips' through the O(2w)–H(2w)···O(3) interaction (Fig. 4 and Table 3). The disordered methanol molecules are attached to the main structure through contacts of the type O(1w)–H(1wA)···O(1M_A).

Structure of $NiS_2O_3(dmph)$ (2)

Compound (2) is also monoclinic, $P2_1/n$. The core of the complex can be thought of as being derived from the close approach of two molecules of complex (1), so as to produce a bonding contact of atoms O(1) and O(2) with the neighbouring Ni^{2+} cation, with simultaneous removal of the aqua ligand. Thus, a dimeric entity results, built around a symmetry centre and formed by two symmetry-related, hexacoordinated Ni^{2+} cations. The polyhedra are thus determined by the usual bidentate dmph, and a now fourfold coordinated thiosulfate (through S(1) and O(2) to a nickel nucleus, and through O(1) and O(2) to its centrosymmetrically related image) thus acting as a double bridge (through O(2) and the S(1)–S(2)–O(1) group) and a bidentate (S(1),O(2)) ligand (Fig. 5). The highly tensioned modes of coordination of both the bidentate dmph base and the quadruply coordinated anion give rise to a rather distorted NiSN$_2$O$_3$ octahedron, hardly amenable of a clear description.
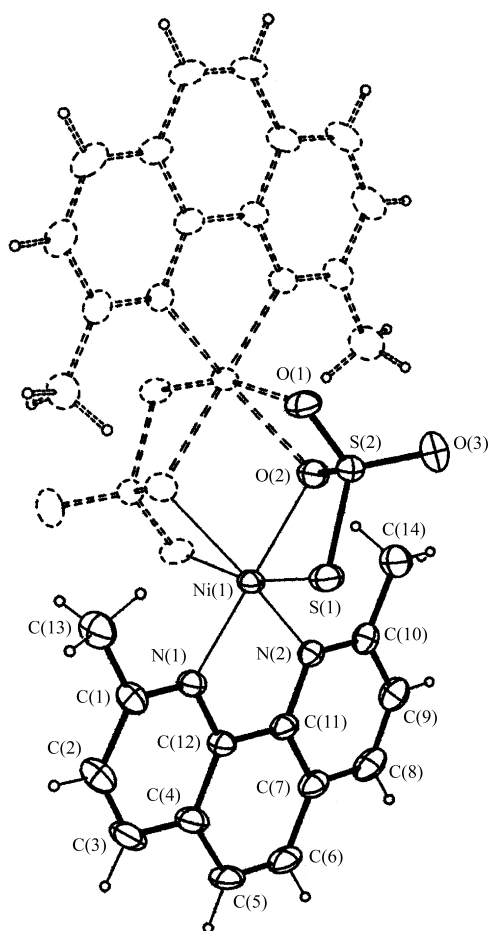

Fig. 5. Molecular drawing of dimer in (2) showing atom labelling. Thermal ellipsoids are drawn at 50% level.

The Ni(1)–S(1) distance (2.409(1) Å) is slightly shorter than those found in other *S*-bonded octahedral complexes and bidentate (S,O) compounds reported in the literature.[23,35] The metal–nitrogen bond lengths are normal for octahedral compounds, while that with oxygen in the 'bite' (2.135(2) Å) is slightly longer than the one found in (1). The two bridging O–Ni bonds are significantly different, 2.151(2) and 2.270(2) Å. This feature is also observed in Ni–S bonds when the thiosulfate bridges through sulfur.[36] The bridging character of the thiosulfate ion through oxygen is unusual and to our knowledge, has not been reported previously.

Coordination of thiosulfate to nickel does not seem to affect the S–S length, as already observed in almost all the structures reported in the literature: this bond distance is almost invariable at *c* 2.00 Å. However, a clear influence on S–O is observed when oxygen is involved in coordination. In this case a gradation is observed, depending on the oxygen participating in none, one or two bonds (1.438(2), 1.486(2), and 1.517(2) Å, respectively).

In spite of the quadruple bridge present, the Ni···Ni distance observed (3.517(1) Å) falls towards the long end of the range recorded in the Cambridge Structural Database for doubly (or higher) bridged Ni···Ni pairs (2.30–3.95 Å).

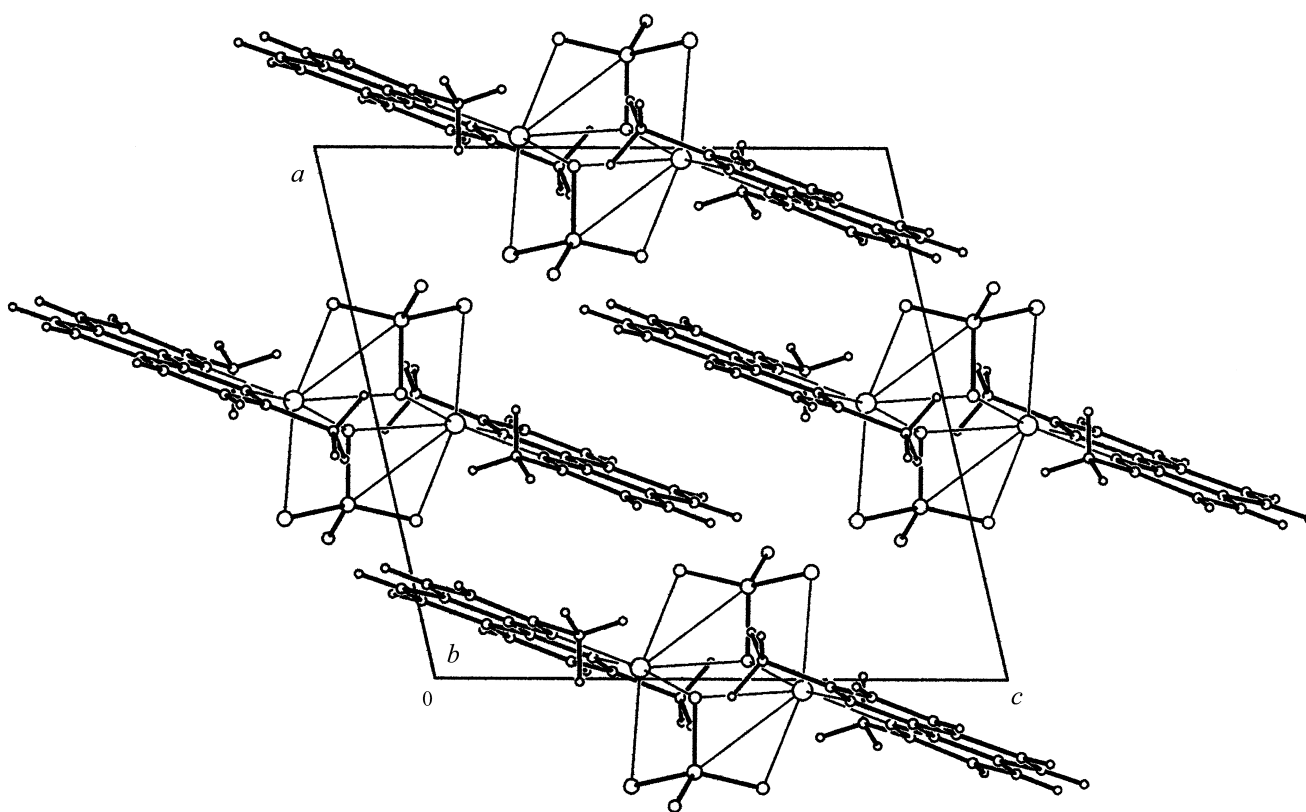The dimers do not interact with each other except through van der Waals forces. However, they are disposed, in a pecu-

Fig. 6. Packing diagram of the dimers in (2).

liar way with all the planar dmph groups parallel to the crystallographic (102) plane (Fig. 6).

Summary

The results reported herein together with those retrieved from the literature allow us to state that the nickel thiosulfate complexes described so far appear with two different ways of coordination of the anion, viz. types *3* and *8* in Fig. 1. In both modes, very small modifications have been observed in the S–S bonds, as compared to those in the free anion. However, S–O bond lengths seem to be sensitive both to the effect of Ni–O bonds when they are present as well as to the existence of strong hydrogen-bonding interactions. The non-linear shape of the bond valence–bond length correlation that leads to the distortion theorem[37] can easily be observed in the S–O bond distances, with an important elongation of those bonds involving oxygens which participate in coordination, and small contractions of those which do not.

Acknowledgments

References

[1] Teng, S. T., Fuess, H., and Bats, J. W., *Acta Crystallogr., Sect. C*, 1984, **40**, 1785, and references therein.

[2] Murdock, A. R., Tyree, T., Otterbein, W., Kinney, L., Carreras, M., Cooper, J. N., and Elder, R. C., *Inorg. Chem.*, 1985, **24**, 3674.

[3] Tang, K., Kastner, M. E., Cooper, J. N. Kanaskie, M., and Monoski, A., *Acta Crystallogr., Sect. C*, 1993, **49**, 1265.

[4] Yamanari, K., Mori, M., Dogi, S., and Fuyuhiro, A., *Inorg. Chem.*, 1994, **33**, 4807.

[5] Yamanari, K., Mori, M., Dogi, S., and Fuyuhiro, A., *Chem. Lett.*, 1993, 1855.

[6] Kastner, M. E., Smith, D. A., Kuzmission, A. G., Cooper, J. N., Tyree, T., and Yearick, M., *Inorg. Chim. Acta*, 1989, **158**, 185.

[7] Baggio, S., Amzel, L. M., and Becka, L. N., *Acta Crystallogr., Sect. B*, 1970, **26**, 1698,

[8] Kubas, G. J., Ryan, R. R., and Kubat-Martin, K. A., *J. Am. Chem. Soc.*, 1989, **111**, 7823.

[9] Edwards, C. F., Griffith, W. P., and Williams, D. J., *J. Chem. Soc., Chem. Commun.*, 1990, 1523.

[10] Edwards, C. F., Griffith, W. P., and Williams, D. J., *J. Chem. Soc., Dalton Trans.*, 1992, 145.

[11] Shcherbakov, V. I., Sarycheva, N. A., Grigor'eva, I. K., Zakharov, L. N., Bochkova, R. I., and Razuvaev, G. A., *Metalloorg. Khim.*, 1990, **3**, 352.

[12] Kubat-Martin, K. A., Kubas, G. J., and Ryan, R. R., *Organometallics*, 1989, **8**, 1910.

[13] Glidewell, C., Lambert, R. J., Hursthouse, M. B., and Motevalli, M., *J. Chem. Soc., Dalton Trans.*, 1989, 2061.

[14] Andreetti, G. D., Cavalca, L., Domiano, P., and Musatti, A., *Ric. Sci.*, 1968, **38**, 1100.

[15] Baggio, R., Baggio, S., Pardo, M. I., and Garland, M. T., *Acta Crystallogr., Sect. C*, 1996, **52**, 820.

16 Toupadakis, A., Kubas, G. J., and Burns, C. J., *Inorg. Chem.*, 1992, **31**, 3810.

17 Hursthouse, M. B., Short, R. L., Kelly, P. F., and Woollins, J. D., *Acta Crystallogr., Sect. C*, 1988, **44**, 1731.

18 Brunner, H., Klement, U., Pfauntsch, J., and Wachter, J., *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 230.

19 Stocker, F. B., and Troester, M. A., *Inorg. Chem.*, 1996, **35**, 3154.

20 Kubas, G. J., and Ryan, R. R., *Inorg. Chem.*, 1984, **23**, 3181.

21 Kim, C. G., and Coucouvanis, D., *Inorg. Chem.*, 1993, **32**, 1881.

22 Murdock, A. R., Tyree, T., Otterbein, W., Kinney, L., Carreras, M., Cooper, J. N., and Elder, R. C., *Inorg. Chem.*, 1985, **24**, 3674.

23 Gasparri, G. F., Mangia, A., Musatti, A., and Nardelli, M., *Acta Crystallogr., Sect. B*, 1969, **25**, 203.

24 Baggio, S., Baggio, R. F., and de Perazzo, P. K., *Acta Crystallogr., Sect. B*, 1974, **30**, 2166.

25 Baggio, R., Baggio, S., Pardo, M. I., and Garland, M. T., *Acta Crystallogr., Sect. C*, 1996, **52**, 1939.

26 Baggio, S., Baggio, R., and Garland, M. T., *Acta Crystallogr., Sect. C*, 1998, **54**, 1099.

27 Baggio, S., Pardo, M. I., Baggio, R., and Garland, M. T., *Acta Crystallogr., Sect. C*, 1997, **53**, 727.

28 Baggio, S., Pardo, M. I., Baggio, R., and Gonzalez, O., *Acta Crystallogr., Sect. C*, 1997, **53**, 1521.

29 Costamagna, J. A., and Levitus, R., *J. Inorg. Nucl. Chem.*, 1966, **28**, 1116.

30 The JCPDS International Center for Diffraction Data, Powder Diffraction File Nos 4-835 and 22-1189, 1992.

31 Sheldrick, G. M., SHELXS97, Program for Crystal Structure Resolution, University of Göttingen, Germany, 1997.

32 Sheldrick, G. M., SHELXL97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.

33 Sheldrick, G. M., SHELXTL-PC, Version 4.2, Siemens Analytical X-Ray Instruments Inc., Madison, Wisconsin, U.S.A., 1991.

34 Nardelli, M., *Comput. Chem.*, 1983, **7**, 95.

35 Freire, E., Baggio, S., Baggio, R. F., and Suescun, L., *Acta Crystallogr., Sect. C*, 1999, **55**, 1780.

36 Baggio, R. F., Baggio, S., Pardo, M. I., and Garland, M. T., *Acta Crystallogr., Sect. C*, 1996, **52**, 1939.

37 Brown, I. D., and Shannon, R. D., *Acta Crystallogr., Sect. A*, 1972, **29**, 266.