DALTON
FULL PAPER

Inter-ligand reactions: *in situ* formation of new polydentate ligands

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Received 21st February 2000, Accepted 9th May 2000
Published on the Web 20th June 2000

Two ligands have been synthesized by derivatisation of cyanuric chloride: 6-(diethylamino)-2,4-disulfanyl-1,3,5-triazine (H_2SSta) **1** and 6-(diethylamino)-2-hydroxo-4-sulfanyl-1,3,5-triazine (H_2OSta) **2** have been characterised by X-ray crystallography, which shows intermolecular hydrogen bonding in the solid state, leading to dimers of **1** and ribbons of **2**. On reaction with metal salts both ligands undergo oligomerisation reactions. Compound **1** reacts with nickel chloride to form a mononuclear complex, $[Ni\{(Sta)S(S_2ta)\}]$ **3**. In **3** two triazine ligands have reacted, to form a tetradentate ligand in which two triazine rings are bridged by a sulfur group, with a co-ordinated disulfide group present on one ring and a co-ordinated thiolate on the second. Compound **2** reacts with cobalt(II) chloride to form a cage complex, $[Co_6NaO(OStaH)_7\{S(Ota)_2\}_2(O_2CPh)_2(H_2O)_2]$ **4**. This complicated structure contains two polydentate ligands formed by linking triazine groups through a bridging sulfur. The cage contains four cobalt(II) and two cobalt(III) sites which are assigned by bond length considerations. The compound $[Co(OSta)_3]$ **5** co-crystallises with **4**, and its structure has also been determined.

The design of ligands underlies much of modern co-ordination chemistry. We have begun exploring the use of S-substituted heterocycles derived from cyanuric acid (1,3,5-triazine-2,4,6-triol) for a number of uses, including solvent extraction, engineering of metal surfaces and synthesis of high spin cages. We believed that these ligands offered the potential for easy functionalisation, allowing us to vary the ligating properties of the molecules systematically. Here we report results involving two related ligands, 6-(diethylamino)-2,4-disulfanyl-1,3,5-triazine (H_2SSta) **1** and 6-(diethylamino)-2-hydroxo-4-sulfanyl-1,3,5-triazine (H_2OSta) **2**. These ligands show an interesting, but difficult co-ordination chemistry as they undergo self-condensation reactions, generating unusual ligands *in situ*. The synthesis of ligands similar to **1** and **2** has been reported previously.[1–3]

Experimental

Preparation of compounds

All reagents, metal salts and ligands were used as obtained from Acros or Aldrich. Analytical data were obtained on a Perkin-Elmer 2400 Elemental Analyser by the University of Edinburgh Microanalytical Service. Mass spectra were obtained by fast atom bombardment (FAB-MS) of samples in a 3-nitrobenzyl alcohol matrix on a Kratos MS50 spectrometer, proton and ^{13}C NMR spectra on a Bruker AM-360 MHz spectrometer.

2,4-Dichloro-6-(diethylamino)-1,3,5-triazine. A solution of cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) (30.6 g, 165.9 mmol) in hot acetone (100 ml) was poured onto a well stirred solution of ice–water (100 ml) to produce a fine slurry. The suspension was cooled in an ice bath to ≈0 °C. Diethylamine (18.5 ml, 166.7 mmol) in a K_2CO_3 solution (165 ml of a 1 M solution, 165 mmol) was added dropwise, maintaining the temperature of the suspension between 0 and 5 °C. The suspension was then stirred at 0–5 °C for a further hour before it was neutralised with 1 M HCl. The suspension was filtered and the precipitate washed with cold distilled water then cold ethanol. The product was dried under vacuum. Yield 24.1 g, 66%. Found: C, 38.4; H, 4.7; N, 25.5. Calc. for $C_7H_{10}Cl_2N_4$: C, 38.0; H, 4.5; N, 25.3%. NMR ($CDCl_3$): ^1H, δ 3.61 (q, 4 H, 2 × CH_2) and 1.20 (t, 6 H, 2 × CH_3); ^{13}C, δ 169.73 (2 × CCl), 163.70 (CN), 42.36 (2 × CH_2) and 12.44 (2 × CH_3).

6-(Diethylamino)-2,4-disulfanyl-1,3,5-triazine (H_2SSta) 1. 2,4-Dichloro-6-(diethylamino)-1,3,5-triazine (3.0 g, 13.6 mmol) was added to an aqueous solution of NaSH (55 ml of a 1 M solution, 55 mmol). The suspension was heated under reflux overnight, then cooled to room temperature, and filtered to remove starting material. The filtrate was acidified with 1 M HCl and the precipitate filtered off. The yield of crude product was 2.6 g. This was recrystallised from ethanol, then dried under vacuum. Yield 1.3 g, 45%. Found: C, 38.8; H, 5.6; N, 25.9. Calc. for $C_7H_{12}N_4S_2$: C, 38.9; H, 5.6; N, 25.9%. NMR (d_6-DMSO): ^1H, δ 12.82 (s, 2 H, very broad, NH), 3.57 (q, 4 H, 2 × CH_2) and 1.10 (t, 6 H, 2 × CH_3); ^{13}C, δ 177.95 (2 × C=S), 148.71 (CN), 42.43 (2 × CH_2) and 13.04 (2 × CH_3). Crystals suitable for X-ray analysis were grown by slow evaporation of an ethanol solution.

4-Chloro-6-diethylamino-1,3,5-triazin-2-one. 2,4-Dichloro-6-(diethylamino)-1,3,5-triazine (15.1 g, 62.3 mmol) was added to a solution of KOH (65 ml of a 2 M solution, 130 mmol) in distilled water (80 ml). The suspension was heated under reflux for 1 hour, then cooled to room temperature and filtered to remove starting material. The filtrate was acidified with 1 M HCl and the white precipitate filtered off. The product was then dried under vacuum. Yield 11.3 g, 89%. Found: C, 41.4; H, 5.5; N, 27.6. Calc. for $C_7H_{11}ClN_4O$: C, 41.5; H, 5.4; N, 27.7%. NMR: ^1H (d_6-DMSO), δ 11.54 (s, 1 H, NH), 11.13 (s, 1 H, NH), 3.53 (dq, 4 H, 2 × CH_2) and 1.09 (dt, 6 H, 2 × CH_3); ^{13}C ($CDCl_3$), δ 158.72 (1C) and 158.25 (2C, overlapping C=O, CCl, CN), 43.20 (CH_2), 42.26 (CH_2), 12.95 (CH_3) and 12.44 (CH_3).

6-(Diethylamino)-2-hydroxo-4-sulfanyl-1,3,5-triazine (H_2OSta) 2. 4-Chloro-6-diethylamino-1,3,5-triazin-2-one (10.0 g, 49.5 mmol) was added to a solution of NaSH (50 ml of a 2 M

DOI: 10.1039/b001404o

solution, 100 mmol). The suspension was heated under reflux for 2 hours, then cooled to room temperature and the product filtered off. The yield of crude product was 8.4 g. This was recrystallised twice from methanol, then dried under vacuum. Yield 4.0 g, 41%. Found: C, 41.7; H, 6.0; N, 27.7. Calc. for $C_7H_{12}N_4OS$: C, 42.0; H, 6.0; N, 28.0%. NMR (d_6-DMSO): ^1H, δ 11.76 (s, 1 H, NH), 11.44 (s, 1 H, NH), 3.5 (broad m, 4 H, 2 × CH_2) and 1.09 (t, 6 H, 2 × CH_3); ^{13}C, δ 183.6 (C=S), 151.82 and 149.36 (CN and C=O), 42.17 (2 × CH_2) and 13.04 (2 × CH_3). Crystals suitable for X-ray analysis were grown by slow evaporation of a methanol solution.

[Ni{(Sta)S(S_2ta)}] 3. Compound **1** was deprotonated by reaction with one equivalent of Na(OMe) in methanol, followed by evaporation to dryness. This sodium salt (1.02 g, 4.2 mmol) was treated with hydrated nickel chloride (0.50 g, 2.1 mmol) in the presence of sodium pivalate (0.52 g, 4.2 mmol) in MeOH (20 ml). The solution was evaporated to dryness, and the resulting black powder redissolved in MeCN to give a dark red solution. Upon standing for several weeks, green-yellow needles formed. Yield: 10%. Found: C, 34.5; H, 3.9; N, 22.9. Calc. for $C_{14}H_{20}N_8NiS_4$: C, 34.5; H, 4.11; N, 23.0%. Crystals suitable for X-ray analysis were grown by redissolving these crystals in CH_2Cl_2 and layering the solution with hexane.

[Co_6NaO(OStaH)$_7${S(Ota)$_2$}$_2$(O_2CPh)$_2$(H_2O)$_2$] 4. Compound **2** was deprotonated by reaction with one equivalent of Na(OMe) in methanol, followed by evaporation to dryness. This sodium salt (1.02 g, 4.6 mmol) was treated with cobalt(II) chloride (0.3 g, 2.3 mmol) and Na(O_2CPh) (0.67 g, 4.6 mmol) in MeOH (50 ml), followed by evaporation to dryness and recrystallisation from MeCN. Yield: 5%. Crystals of **4** suitable for X-ray diffraction studies grew from MeCN after a period of 2 weeks. The mother liquor was allowed to stand, and after a further period of 9 months green crystals of [Co(OSta)$_3$] **5** formed in very low yield.

Crystallography

Crystal data and data collection and refinement parameters for compounds **1**–**5** are given in Table 1, selected bond lengths and angles in Tables 2–4.

Data collection and processing. With the exception of compound **4**, all data were collected with Cu-Kα radiation on a Stoe Stadi-4 diffractometer. Absorption corrections for **3** and **5** were performed by Gaussian integration following refinement of the crystal shape against a set of ψ scans (Stoe X-shape);[4] the correction for **2** was performed by conventional application of ψ-scan data (SHELXTL),[5] while that for **4** used the multi-scan procedure SORTAV.[6] Crystals of **4** diffracted weakly, and data were collected using a Nonius Kappa-CCD diffractometer with a rotating anode Mo-Kα source at the EPSRC National Crystallography Service; data to $2\theta = 45°$ were used for refinement.

Structure analysis and refinement. The structure of compound **3** was solved by Patterson methods (DIRDIF);[7] all others were solved by direct methods (SHELX 97).[8] Refinement against F^2 was performed using SHELX 97; the program PLATON[9] was used extensively for structural analysis. Hydrogen atoms were placed in calculated positions and allowed to ride on their parent atoms.

In compounds **1** and **2** the NEt_2 groups are disordered over two conformations. The relative occupancies were refined with all NEt_2 restrained to be geometrically similar. In **1** only the full-weight atoms were refined with anisotropic displacement parameters (adps). Perhaps because of the rather low crystal quality, ψ-scan data were very noisy and so an absorption correction based on the model (SHELXA[8]) was applied during refinement. In **3** refinement of an ordered model revealed a ΔF map peak with a height of *ca.* 2 e Å^{-3} next to Ni1. This and other weaker difference map features were interpreted as arising from orientational disorder of the whole complex *via* a twofold rotation about an axis which passes approximately through Ni1 and S6AB. The minor nickel position and two plausible sulfur positions were used to define a complete alternative orientation for the planar part of the complex; minor-weight methyl positions were located in a difference synthesis calculated about the locus of possible carbon positions. The minor fragment was initially treated as a rigid body, but was later refined with related bonds and angles in the two fragments subject to similarity restraints. One NEt_2 group in the major component is also orientationally disordered. Such features are sometimes said to arise from twinning. Pseudo twofold axes are present in the [307], [205], [100] and [409] directions, but attempts to refine the model using these (rather unlikely) twin laws led to no improvement. The fact that all reflections located in the initial search of reciprocal space could be satisfactorily indexed with one orientation matrix supports this, and suggests that the observed effects are either due to disorder (the model presented here) or to the existence of a very much larger super-cell. All atoms in the major fragment were refined with adps; an isotropic displacement parameter was refined for the minor Ni atom, while all other minor-component atoms were modelled with a common U_{iso}. In **4**, similarity restraints were applied to chemically equivalent ligands and to the solvent molecules, several of which are part-weight. Hydrogen atoms were placed on N or O to optimise hydrogen bonding. Adps were refined for Co, S, O and Na. Crystals of **5** diffracted very weakly, and data could be collected only to a resolution of 1.2 Å ($2\theta = 80°$ with Cu-Kα radiation). The structure is unusually complicated with eight crystallographically independent mononuclear complexes in the asymmetric unit; the program MISSYM[10] was used to show that the model presented here contains neither higher symmetry nor missed translational symmetry. Similarity restraints were applied to all chemically equivalent bond lengths and angles during refinement. Hydrogen atoms were not placed on the water of crystallisation. Adps were refined for Co, S and O only.

CCDC reference number 186/1974.

See http://www.rsc.org/suppdata/dt/b0/b001404o/ for crystallographic files in .cif format.

Results

Synthesis and structure of ligands

Both 6-(diethylamino)-2,4-disulfanyl-1,3,5-triazine (H_2SSta) **1** and 6-(diethylamino)-2-hydroxo-4-sulfanyl-1,3,5-triazine (H_2-OSta) **2** can be made from cyanuric chloride, *via* synthesis of 2,4-dichloro-6-diethylamino-1,3,5-triazine (Scheme 1). The presence of the amine group is thought to stabilise the molecule from unwanted hydrolysis and solvolysis reactions.[1] Compound **1** was obtained by straightforward reaction of 2,4-dichloro-6-diethylamino-1,3,5-triazine with NaSH, and **2** by sequential treatment with NaOH, giving 2-chloro-4-hydroxy-6-diethylamino-1,3,5-triazine, followed by reaction with NaSH to displace the final chloro group.

In both cases crystals suitable for X-ray diffraction were grown from evaporation of an EtOH solution for compound **1**, and from evaporation of MeOH for **2**. Both molecules are involved in intermolecular hydrogen bonding in the solid state. In **1**, N(1) and S(6) form a "head-to-tail" pair of interactions with the equivalent atoms in a neighbouring molecule leading to a dimer (Fig. 1). The N · · · S distance of 3.272(5) Å is similar to that found in 2,4,6-trithiocyanuric acid.[11] No further hydrogen bonds are found involving the second S atom [S(2)] in the molecule. A similar "head-to-tail" pair is found in **2**, involving hydrogen bonding between S(6) and N(1) in neighbouring

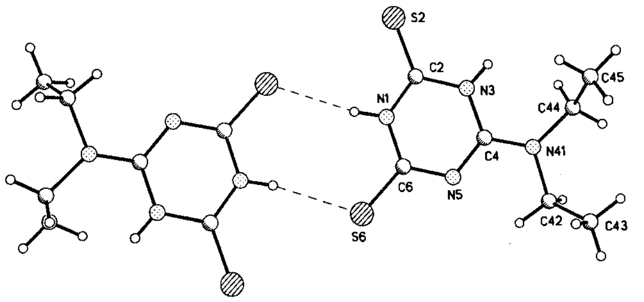
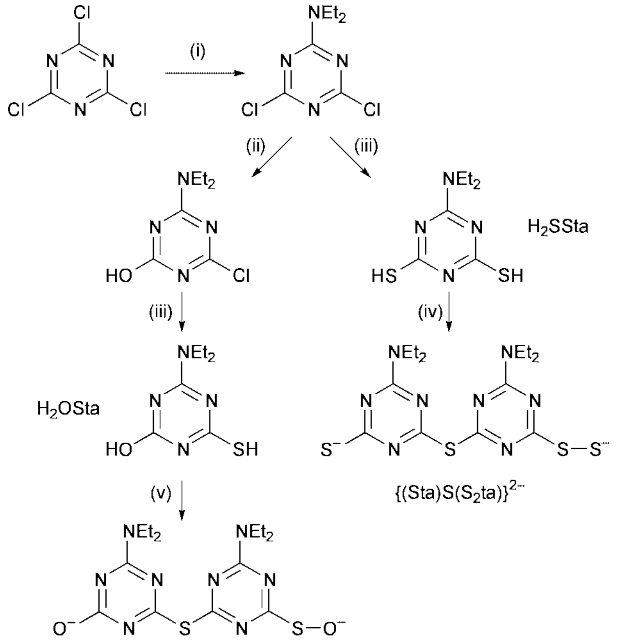


Fig. 1 The structure of compound **1** in the crystal. The hydrogen bonds which form dimers in the solid state are indicated by dashed lines. Selected bond lengths: N(1)–C(2) 1.330(7), N(1)–C(6) 1.367(6), C(2)–N(3) 1.384(7), C(2)–S(2) 1.654(5), N(3)–C(4) 1.365(7), C(4)–N(41) 1.318(7) and C(4)–N(5) 1.342(7) Å.



Scheme 1 *Reagents*: (i) $HNEt_2$, K_2CO_3; (ii) KOH; (iii) NaSH; (iv) $NiCl_2{\cdot}6H_2O$, NaO_2CMe_3; (v) $CoCl_2$, NaO_2CPh.

molecules, but in addition there is a "head-to-tail" interaction between O(2) and N(3) involving a third group, leading to hydrogen-bonded strands within the structure (Fig. 2). The N···S distance is 3.339(5) Å while the N···O distance of 2.799(5) Å is similar to those found in dimers of 2-pyridone derivatives.[12] In both **1** and **2** the H atoms were placed in calculated positions in the structure (attached to the more electronegative N atom with a hydrogen bond to the neighbouring S atom), therefore it is not possible from the structure to state whether the mercapto or thione tautomer is present. In **2** the C–O bond length (1.22 Å) suggests the keto tautomer is present rather than the hydroxo, and therefore again the H atom was attached to the N atom from the heterocycle for refinement purposes.

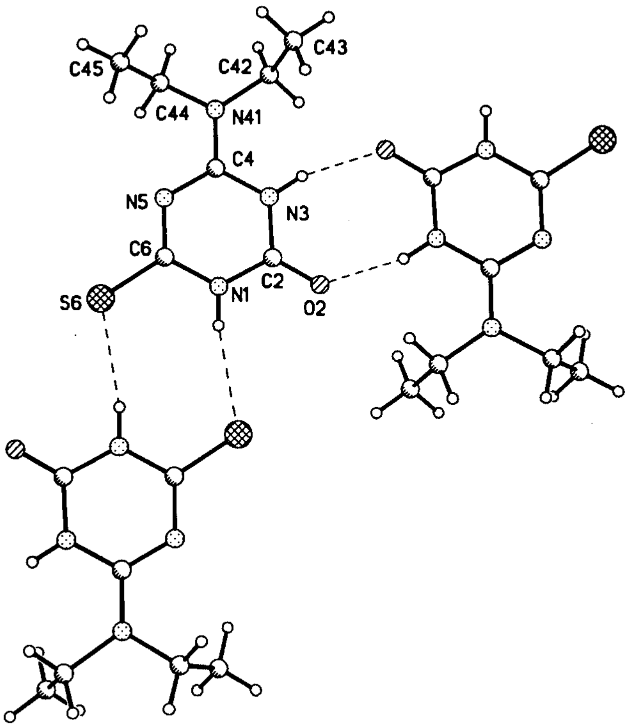


Fig. 2 The structure of compound **2** in the crystal. Three molecules are shown to illustrate the hydrogen bonding (dashed lines) within the structure. Selected bond lengths: N(1)–C(2) 1.364(5), N(1)–C(6) 1.377(5), C(2)–O(2) 1.215(5), C(2)–N(3) 1.365(5), N(3)–C(4) 1.368(5), C(4)–N(41) 1.318(6), C(4)–N(5) 1.332(5), N(5)–C(6) 1.337(5) and C(6)–S(6) 1.679(4) Å.

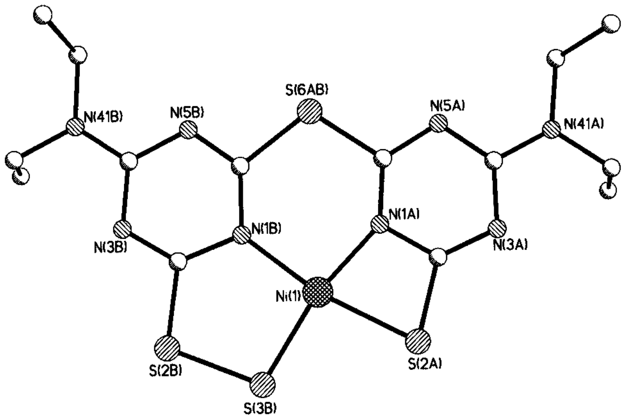


Fig. 3 The structure of compound **3** in the crystal.

Synthesis and structure of [Ni{(Sta)S(S_2ta)}] 3

The sodium salt of compound **1** is formed by reaction of H_2SSta with Na(OMe), and this was treated with nickel(II) chloride hexahydrate in the presence of sodium pivalate. We have previously found that addition of carboxylate salts can solubilise otherwise intractable reactants,[13] which assists in formation of crystalline material, even where the carboxylate is not incorporated in the final product. Evaporation of the MeOH solution gave a black powder. This was extracted with MeCN, to give a dark red solution, from which green-yellow needles of **3** grow after several weeks. It was necessary further to recrystallise this material from CH_2Cl_2–hexane to produce yellow blocks suitable for X-ray studies. The need to carry out two low-yielding recrystallisations leads to formation of **3** in low (10%) yield. We believe the crystalline material grown from MeCN is similar to **3**, which would raise the yield to 30%, but we have not been able to characterise the dark red solution unambiguously.

Elemental analysis suggests one nickel bound to two ligands, but X-ray analysis shows that while this stoichiometry is maintained the two ligands have reacted to produce a complex of formula [Ni{(Sta)S(S_2ta)}] **3** (Fig. 3). Significant bond lengths and angles are given in Table 2. The nickel is four-co-ordinate, bound to N-donors from the triazines and two sulfur atoms, one from the disulfide and the second from the thiol group of a triazine. The resulting co-ordination geometry is distorted square planar, with *cis* angles varying from 73.5 to 96.0° and *trans* angles of around 169°. The bond lengths to the Ni show considerable variation. The shortest is the Ni–N(1A) bond [1.841(5) Å], to the N atom of the triazine to which the thiol group is attached. This is considerably shorter than the Ni–N(1B) bond [1.913(5) Å] to the other triazine. There is also a

Table 1 Experimental data for the X-ray diffraction studies of compounds **1**–**5**

	1	**2**	**3**	**4**	**5**
Formula	$C_7H_{12}N_4S_2$	$C_7H_{12}N_4OS$	$C_{14}H_{20}N_8NiS_4$	$C_{91}H_{131}Co_6N_{44}NaO_{18}S_9\cdot 8C_2H_3N$	$C_{168}H_{259}Co_8N_{96}O_{27}S_{24}\cdot 11C_2H_3N\cdot 3CH_4O\cdot 2H_2O$
M	216.3	200.3	487.3	3122.9	5880.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/n$	$Pbcn$
a/Å	9.030(2)	7.789(3)	7.5234(15)	19.6882(8)	53.242(11)
b/Å	13.949(4)	7.043(2)	16.689(3)	19.7229(8)	33.671(7)
c/Å	9.394(2)	17.452(8)	16.472(3)	39.7227(18)	33.537(7)
β/°	111.079(13)	93.36(4)	101.145(17)	94.844(2)	
U/Å^3	1104.1(5)	955.7(7)	2029.2(7)	15369.6(11)	60122(21)
T/K	295(2)	220.0(2)	220.0(2)	150.0(2)	220.0(2)
Z	4	4	4	4	8
μ/mm^{-1}	4.083	2.764	5.381	0.830	5.539
Unique data	1925	1647	3575	19775	18245
Unique data with $F_o > 4\sigma(F_o)$	1568	1446	2542	6930	7035
$R1$, $wR2$[a]	0.0989, 0.3011	0.0758, 0.2224	0.0740, 0.2095	0.0998, 0.3073	0.1373, 0.4236

[a] $R1$ based on observed data, $wR2$ on all unique data.

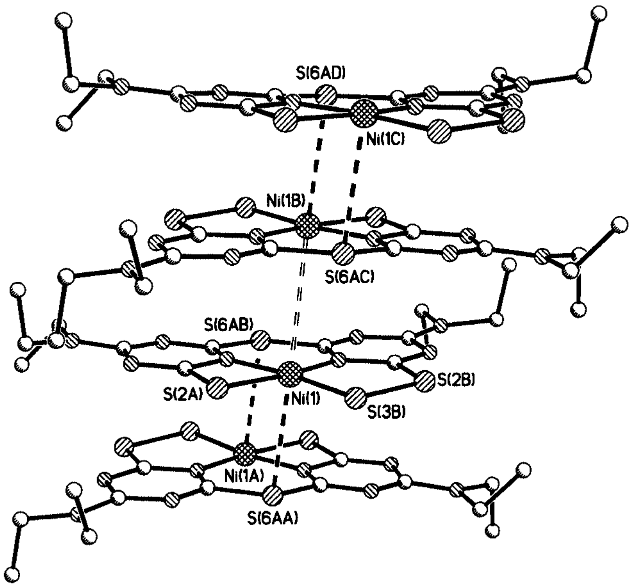


Fig. 4 A view perpendicular to the stacking of molecules of compound **3** in the crystal. The Ni···S contacts within "dimers" are shown as filled dashed lines; the Ni···Ni contact between "dimers" is shown as an open dashed line.

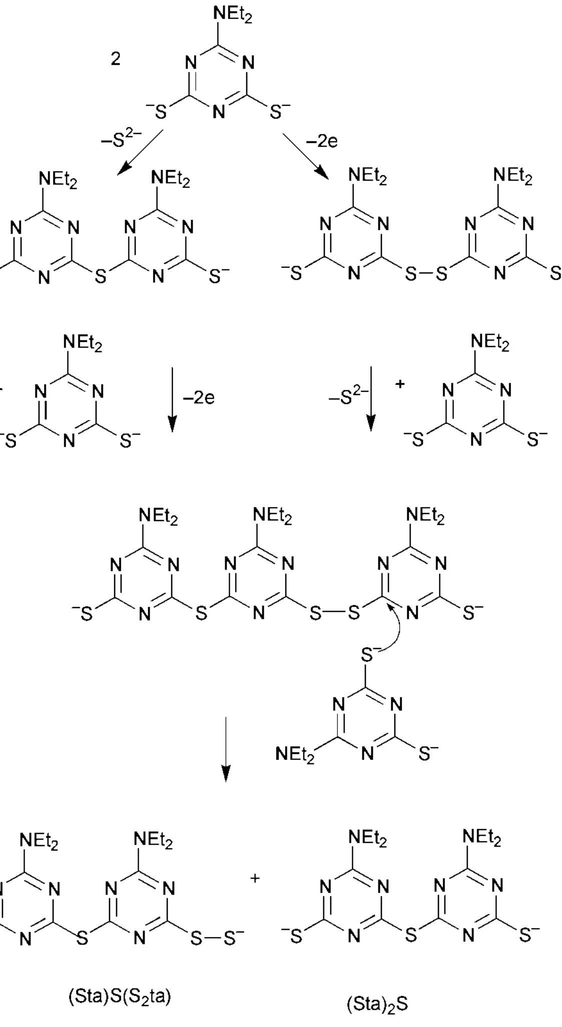
significant difference between the two Ni–S bonds, with the bond to the disulfide sulfur, Ni–S(3B), shorter at 2.131(2) Å than the bond to the thiol sulfur [2.240(2) Å]. The Ni–S(disulfide) bond is typical of previous examples containing this feature,[14] as is the S–S bond of 2.049(3) Å.

The molecules of compound **3** stack in the solid state (Fig. 4). The most significant inter-molecule interactions are between the Ni [*e.g.* Ni(1) or Ni(1A)] and the bridgehead sulfur [*e.g.* S(6AA) or S(6AB)]. This contact of 3.27 Å is close to the sum of the van der Waals radii of the two elements. The arrangement of the molecules of **3** is such that the triazine rings are directly above one another within these dimers. The distance between the centroids of neighbouring triazines is 3.41 Å, which represents a weak "graphitic" interaction. These weak interactions create "dimers" within the stacks. The closest "inter-dimer" interaction is a Ni···Ni contact of 3.58 Å [Ni(1)···Ni(1B) in Fig. 4].

All routes to the ligand $\{(Sta)S(S_2ta)\}^{2-}$ require a multi-step mechanism. One possibility is shown in Scheme 2. The first two steps proposed are formation of a disulfide bridge between two triazine ligands, and nucleophilic substitution reaction involving displacement of one thiol from an SSta ligand by a thiol from a second triazine. The same product results which-

Table 2 Selected bond lengths (Å) and angles (°) for compound **3**

Ni(1)–N(1A)	1.841(5)	Ni(1)–N(1B)	1.913(5)
Ni(1)–S(3B)	2.1307(18)	Ni(1)–S(2A)	2.240(2)
S(2B)–S(3B)	2.049(3)		
N(1A)–Ni(1)–N(1B)	96.0(2)	N(1A)–Ni(1)–S(3B)	168.27(19)
N(1B)–Ni(1)–S(3B)	95.68(15)	N(1A)–Ni(1)–S(2A)	73.47(18)
N(1B)–Ni(1)–S(2A)	169.46(15)	S(3B)–Ni(1)–S(2A)	94.86(8)
C(2B)–S(2B)–S(3B)	103.8(2)	S(2B)–S(3B)–Ni(1)	100.21(9)



Scheme 2 Possible reaction path to give $\{(Sta)S(S_2ta)\}^{2-}$.

Table 3 Selected bond lengths (Å) for compound **4**

Co(1)–O(6A)	2.039(10)	Co(1)–O(11)	2.066(9)
Co(1)–O(6J)	2.069(9)	Co(1)–O(6K)	2.096(9)
Co(1)–O(124)	2.132(9)	Co(1)–O(6C)	2.152(9)
Co(2)–O(21)	1.954(10)	Co(2)–N(1B)	2.006(11)
Co(2)–N(1A)	2.009(11)	Co(2)–O(124)	1.977(9)
Co(3)–O(6F)	2.058(9)	Co(3)–O(6B)	2.080(9)
Co(3)–O(2W)	2.080(9)	Co(3)–O(6D)	2.101(9)
Co(3)–O(1W)	2.109(9)	Co(3)–O(6H)	2.136(9)
Co(4)–O(22)	2.010(9)	Co(4)–O(124)	2.021(9)
Co(4)–N(1D)	2.023(11)	Co(4)–N(1C)	2.035(11)
Co(4)–O(12)	2.496(9)	Co(5)–N(1I)	1.956(10)
Co(5)–N(1K)	1.960(10)	Co(5)–S(2H)	2.277(5)
Co(5)–S(2J)	2.286(4)	Co(5)–S(2I)	2.296(5)
Co(5)–S(2K)	2.320(4)	Co(6)–N(1G)	1.929(10)
Co(6)–N(1F)	1.939(10)	Co(6)–N(1E)	1.945(10)
Co(6)–S(2F)	2.280(4)	Co(6)–S(2G)	2.283(4)
Co(6)–S(2E)	2.302(5)	Na(1)–O(6E)	2.333(10)
Na(1)–O(6I)	2.339(10)	Na(1)–O(6F)	2.468(10)
Na(1)–O(6H)	2.488(10)	Na(1)–O(22)	2.560(10)
Na(1)–O(6G)	2.652(11)	Na(1)–O(6D)	2.995(11)

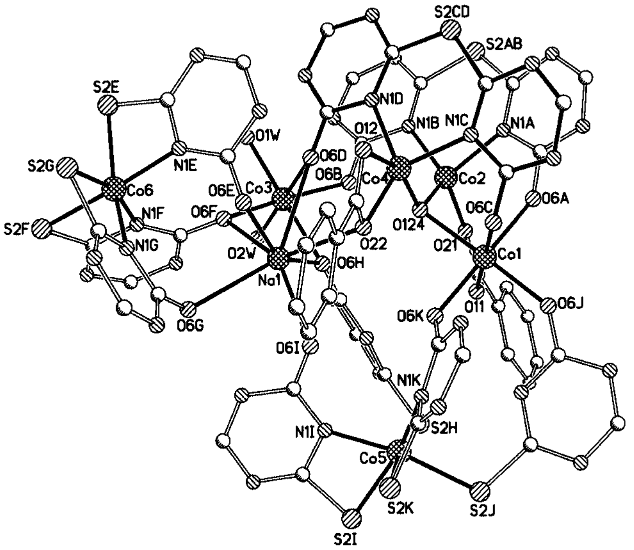


Fig. 5 The structure of compound **4** in the crystal. The NEt_2 groups attached to the triazine rings have been omitted for clarity.

ever step is taken first. The final step is then nucleophilic displacement of the disulfide by an incoming SSta group, giving $\{(Sta)S(S_2ta)\}^{2-}$ and $\{(Sta)_2S\}^{2-}$ as products. While the former is found in formation of the complex **3**, a product related to the latter group is found in **4** (see below). Formation of the disulfide bridge is an oxidation of the ligand, which is presumably carried out by atmospheric dioxygen. We have not been able to improve the yield of **3** by bubbling dry oxygen through the solution.

Synthesis and structure of $[Co_6NaO(OStaH)_7\{S(Ota)_2\}_2(O_2CPh)_2(H_2O)_2]$ 4 and $[Co(OStaH)_3]$ 5

Reaction of Na(OStaH) with cobalt(II) chloride and Na-(O_2CPh) in MeOH, followed by evaporation to dryness and recrystallisation from MeCN, gives another product in which the thiol groups attached to the triazine have reacted with one another. Here the product, as characterised by X-ray diffraction, is a great deal more complicated to describe than **3** (Fig. 5). As in the synthesis of **3**, the yield of **4** is poor due to the recrystallisation step. The major product is a black solid which forms before **4** and which, despite repeated efforts to crystallise, has not yet been characterised unambiguously. The formula of the cage found within the crystalline material is $[Co_6NaO(OStaH)_7\{S(Ota)_2\}_2(O_2CPh)_2(H_2O)_2]$ **4**. Significant bond lengths and angles are given in Tables 3 and 4 respectively.

Table 4 Selected bond angles (°) for compound **4**

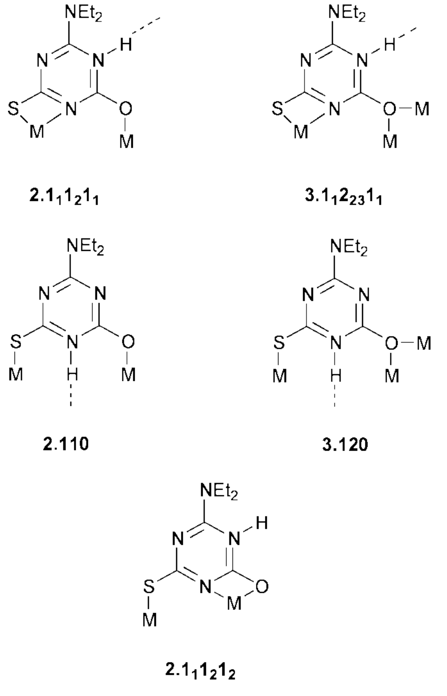
O(6A)–Co(1)–O(11)	97.5(4)	O(6A)–Co(1)–O(6J)	91.4(4)
O(11)–Co(1)–O(6J)	89.5(4)	O(6A)–Co(1)–O(6K)	175.4(4)
O(11)–Co(1)–O(6K)	87.1(4)	O(6J)–Co(1)–O(6K)	87.9(4)
O(6A)–Co(1)–O(124)	89.7(3)	O(11)–Co(1)–O(124)	88.1(3)
O(6J)–Co(1)–O(124)	177.5(4)	O(6K)–Co(1)–O(124)	91.2(3)
O(6A)–Co(1)–O(6C)	85.7(4)	O(11)–Co(1)–O(6C)	176.4(4)
O(6J)–Co(1)–O(6C)	88.8(4)	O(6K)–Co(1)–O(6C)	89.7(3)
O(124)–Co(1)–O(6C)	93.6(4)	O(21)–Co(2)–O(124)	106.2(4)
O(21)–Co(2)–N(1B)	111.4(4)	O(124)–Co(2)–N(1B)	122.7(4)
O(21)–Co(2)–N(1A)	112.8(4)	O(124)–Co(2)–N(1A)	109.6(4)
N(1A)–Co(2)–N(1B)	93.7(4)	O(6F)–Co(3)–O(6B)	170.4(4)
O(6F)–Co(3)–O(2W)	94.0(4)	O(6B)–Co(3)–O(2W)	92.9(4)
O(6F)–Co(3)–O(6D)	84.6(4)	O(6B)–Co(3)–O(6D)	88.4(4)
O(2W)–Co(3)–O(6D)	178.5(4)	O(6F)–Co(3)–O(1W)	94.1(4)
O(6B)–Co(3)–O(1W)	92.9(4)	O(2W)–Co(3)–O(1W)	87.3(4)
O(6D)–Co(3)–O(1W)	93.3(4)	O(6F)–Co(3)–O(6H)	86.9(4)
O(6B)–Co(3)–O(6H)	86.1(4)	O(2W)–Co(3)–O(6H)	92.1(3)
O(6D)–Co(3)–O(6H)	87.3(3)	O(6D)–Co(3)–O(6H)	178.9(4)
O(22)–Co(4)–O(124)	100.5(4)	O(22)–Co(4)–N(1D)	132.6(4)
O(124)–Co(4)–N(1D)	104.4(4)	O(22)–Co(4)–N(1C)	120.8(4)
O(124)–Co(4)–N(1C)	101.3(4)	N(1D)–Co(4)–N(1C)	93.0(4)
O(22)–Co(4)–O(12)	57.9(4)	O(124)–Co(4)–O(12)	158.0(4)
N(1D)–Co(4)–O(12)	94.7(4)	N(1C)–Co(4)–O(12)	88.3(4)
N(1I)–Co(5)–N(1K)	96.2(4)	N(1I)–Co(5)–S(2H)	96.0(3)
N(1K)–Co(5)–S(2H)	108.7(3)	N(1I)–Co(5)–S(2J)	168.3(3)
N(1K)–Co(5)–S(2J)	95.4(3)	S(2H)–Co(5)–S(2J)	82.04(16)
N(1I)–Co(5)–S(2I)	71.4(3)	N(1K)–Co(5)–S(2I)	159.2(3)
S(2H)–Co(5)–S(2I)	89.62(17)	S(2J)–Co(5)–S(2I)	96.99(16)
N(1I)–Co(5)–S(2K)	93.0(3)	N(1K)–Co(5)–S(2K)	70.6(3)
S(2H)–Co(5)–S(2K)	171.01(17)	S(2J)–Co(5)–S(2K)	89.08(16)
S(2I)–Co(5)–S(2K)	92.85(17)	N(1G)–Co(6)–N(1F)	98.2(4)
N(1G)–Co(6)–N(1E)	95.3(4)	N(1F)–Co(6)–N(1E)	101.2(4)
N(1G)–Co(6)–S(2F)	93.9(3)	N(1F)–Co(6)–S(2F)	72.0(3)
N(1E)–Co(6)–S(2F)	169.3(3)	N(1G)–Co(6)–S(2G)	71.6(3)
N(1F)–Co(6)–S(2G)	162.0(3)	N(1E)–Co(6)–S(2G)	94.6(3)
S(2F)–Co(6)–S(2G)	93.46(16)	N(1G)–Co(6)–S(2E)	161.0(3)
N(1F)–Co(6)–S(2E)	97.4(4)	N(1E)–Co(6)–S(2E)	71.0(3)
S(2F)–Co(6)–S(2E)	101.22(16)	S(2G)–Co(6)–S(2E)	95.76(17)
O(6E)–Na(1)–O(6I)	125.8(4)	O(6E)–Na(1)–O(6F)	92.7(4)
O(6I)–Na(1)–O(6F)	132.1(4)	O(6E)–Na(1)–O(6H)	147.7(4)
O(6I)–Na(1)–O(6H)	83.7(3)	O(6F)–Na(1)–O(6H)	71.2(3)
O(6E)–Na(1)–O(22)	76.2(3)	O(6I)–Na(1)–O(22)	86.7(3)
O(6F)–Na(1)–O(22)	134.2(4)	O(6H)–Na(1)–O(22)	94.9(3)
O(6E)–Na(1)–O(6G)	77.8(3)	O(6I)–Na(1)–O(6G)	79.6(3)
O(6F)–Na(1)–O(6G)	82.8(3)	O(6H)–Na(1)–O(6G)	125.4(4)
O(22)–Na(1)–O(6G)	135.0(4)	O(6E)–Na(1)–O(6D)	84.0(3)
O(6I)–Na(1)–O(6D)	139.6(4)	O(6F)–Na(1)–O(6D)	60.7(3)
O(6H)–Na(1)–O(6D)	63.7(3)	O(22)–Na(1)–O(6D)	73.9(3)
O(6G)–Na(1)–O(6D)	138.2(3)		

The ligand reaction is more straightforward, and not all ligands present have condensed. Two ligands, $\{S(Ota)_2\}^{2-}$, see Scheme 1, are found in which a sulfur from one triazine has displaced a sulfur from a second, thus linking two oxygen-substituted triazines. These ligands lie almost co-planar within the cage [see ligands involving S(2AB), N(1B), O(6B), N(1A), O(6A) and S(2CD), N(1D), O(6D), N(1C), O(6C)] and forming six-membered chelate rings with Co(2) and Co(4) respectively, using triazine nitrogen donors. One oxygen atom [O(6A) and O(6C)] from each binds to Co(1), and the second O-donor [O(6B) and O(6D)] from each binds to Co(3). A difference is that the O atoms bind to Co(1) in a *syn* fashion, but to Co(3) as *anti*. A μ_3-oxide [O(124)] also bridges Co(2), Co(4) and Co(1).

While this segment of the cage is comparatively orderly, the remaining three metal sites are irregularly distributed. Co(5) is attached to the cage through two $OStaH^-$ ligands, which bind to Co(1) through the O-donor [O(6K) or O(6J)] and to Co(5) through the sulfur [S(2K) or S(2J)]. The N atom between the two exocyclic groups is protonated, and in both cases is involved in hydrogen bonds. Co(6) is attached to three $OSta^-$ ligands, with each ligand chelating to Co(6) through the S atom and the N(1) site of the triazine, to give a *fac*-octahedral geometry. This is a similar mode of co-ordination to that observed for cobalt co-ordinated to 2-sulfanylpyridine. The tris-chelate around Co(6) thus has three O atoms to act as donors to other metals, and these [O(6E), O(6F) and O(6G)] all bind to a sodium atom [Na(1)] with one of the O atoms [O(6F)] bridging further to Co(3). The sodium site is bridged to Co(5) through two OSta$^-$ ligands, both of which bind to Na through the O-donor [O(6I) or O(6H)], while one co-ordinates to Co(5) through both N- and S-donors [N(1I) and S(2I)], while the second binds to Co(5) through the exocyclic sulfur alone [S(2H)]. Two benzoates are also found in the structure. One chelates to Co(1) through O(11) and O(21), and also bridges to Co(2) through O(21). The second chelates to Co(4) through O(12) and O(22), with O(22) forming a bridge to Na(1).

The metal co-ordination sites are extremely varied. Co(1) and Co(3) are each bound to six O-donors, and have regular octahedral geometries. Co(2) is bound to two N- and two O-donors, with a distorted tetrahedral geometry. Co(4) has three O- and two N-donors in its co-ordination sphere. The Co(4)–O(12) bond is significantly longer than the remaining four bonds, and the geometry is best regarded as a capped tetrahedron. Co(5) is bound to the N- and S-donors of two chelating OStaH$^-$ ligands, and to two further S atoms. The geometry is based on octahedral, but severely distorted by the two chelating groups. Co(6) is bound to the N- and S-donors of three chelating OStaH$^-$ ligands. The geometry is distorted octahedral. The sodium site has seven O-donors within bonding distance, with a predictably distorted geometry.

Assigning charge is not straightforward in compound **4**. Consideration of the bridging modes and hydrogen bonding involving the OStaH$^-$ ligands led us to consider all of them to be singly deprotonated anions. These ligands display four binding modes, two which involve binding through a triazine nitrogen, and two which do not (Scheme 3). First, chelating to one metal through the N(1) position and the exocyclic sulfur, while bridging to a second metal through the O-donor. This mode is displayed by two of the three OSta$^-$ ligands attached to Co(6), and by two of the four ligands bound to Co(5). The second mode is closely related, differing in that the O-donor binds to two metals. This mode is displayed exclusively by one ligand attached to Co(6) through N(1F) and S(2F), while O(6F) bridges between Co(3) and Na(1). The third co-ordination mode involves bridging between two metals, with the S atom [S(2J)] attached to one metal [Co(5)] and the O atom [O(6J)] to a second [Co(1)]. The fourth mode is very similar, with the S atom [S(2H)] bound to one metal [Co(5)], and the oxygen [O(6H)] bridging between two metals [Co(3) and Na(1)]. We will return to these bonding modes in the Discussion.



Scheme 3 Five possible bonding modes for OStaH$^-$: the first four modes are displayed in compound **4**. The numbers below each bonding mode refer to the Harris notation (see text). The fifth mode $[2.1_11_21_2]$ is included to show how Harris notation distinguishes between possible binding modes (*cf.* $[2.1_11_21_1]$). The dashed lines to H atoms indicate hydrogen bonds.

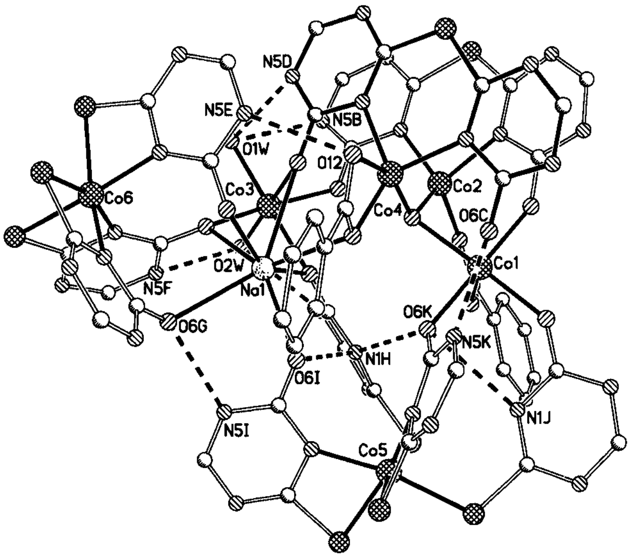


Fig. 6 The intra-molecular hydrogen bonding in compound **4**, shown as dashed lines. N$\cdots$O contacts: N(5E)$\cdots$O(12) 2.859, N(5F)$\cdots$O(2W) 2.690, N(5I)$\cdots$O(6G) 2.785, N(1J)$\cdots$O(6K) 2.980, N(1H)$\cdots$O(6K) 2.854, N(1H)$\cdots$O(6I) 2.973, N(5K)$\cdots$O(6C) 2.731, O(1W)$\cdots$N(5D) 2.791, O(1W)$\cdots$N(5B) 2.912, O(2W)$\cdots$N(5H) 2.723 Å. Av. esd: 0.012 Å.

Within compound **4** there is a complicated series of hydrogen bonds (Fig. 6). For the ligands which show the last two binding modes, the N(1) nitrogen of the triazine is protonated and acts as a hydrogen-bond donor, with the hydrogen-bond acceptor being the exocyclic oxygen of a neighbouring OSta$^-$ ligand. The N$\cdots$O distances vary from 2.85 to 2.98 Å. For the ligands where N(1) is bound, the N(5) nitrogen (*i.e.* the nitrogen *para* to the exocyclic sulfur) is protonated, and acts as a hydrogen-bond donor, with the acceptor an oxygen derived from a co-ordinated water, a benzoate or an OSta$^-$ ligand. Here the N$\cdots$O distances vary from 2.69 to 2.86 Å. The final hydrogen-bonds involve the condensed $\{S(Ota)_2\}^{2-}$ ligands, where a water molecule [O(1W)] is the donor to the N(5) nitrogen in the triazine ring nearest [N$\cdots$O distances 2.79 and 2.91 Å].

This assignment of charge to the OStaH$^-$ ligands requires that two of the six cobalt sites in compound **4** are Co^{III}, while the remaining four are Co^{II}. While Co(2) and Co(4) can probably be assigned as Co^{II} due to their approximately tetrahedral co-ordination geometry, assigning oxidation states to the other sites is more complicated. The similarities between the bond lengths at the Co(5) and Co(6) sites [Co–S 2.277–2.320(5), Co–N 1.929–1.960(10) Å], and the bond lengths in tris(2-pyridinethiolato)cobalt(III) [Co–S 2.285–2.307(5), Co–N 1.904–1.938(6) Å],[15] rather than the bond lengths in the anionic complex tris(2-pyridinethiolato)cobaltate(II) [Co–S 2.552–2.585(6), Co–N 2.094–2.135(8) Å],[16] supports assignment of these centres to the higher oxidation state. This assignment leaves Co(1) and Co(3) as Co^{II}. It is interesting that the higher oxidation state is bound to the "softer" S- and N-donor groups, while Co(1) and Co(3), in the lower oxidation state, are bound exclusively to O-donors.

Further evidence for this assignment of oxidation state comes from the crystallisation of [Co(OStaH)$_3$] **5** from the reac-

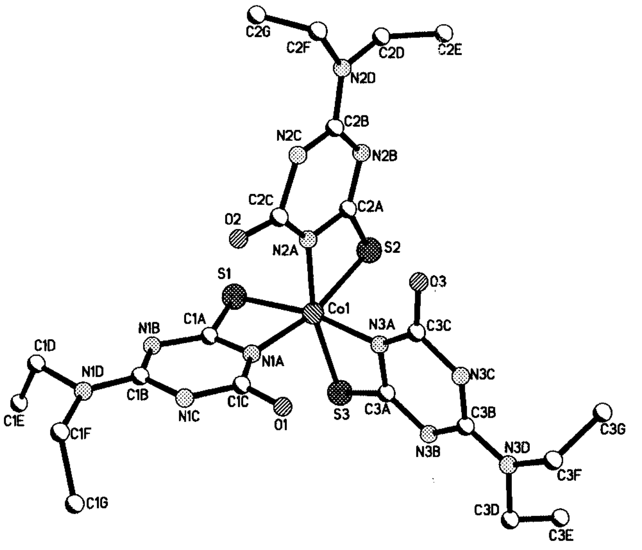


Fig. 7 The structure of compound **5** in the crystal.

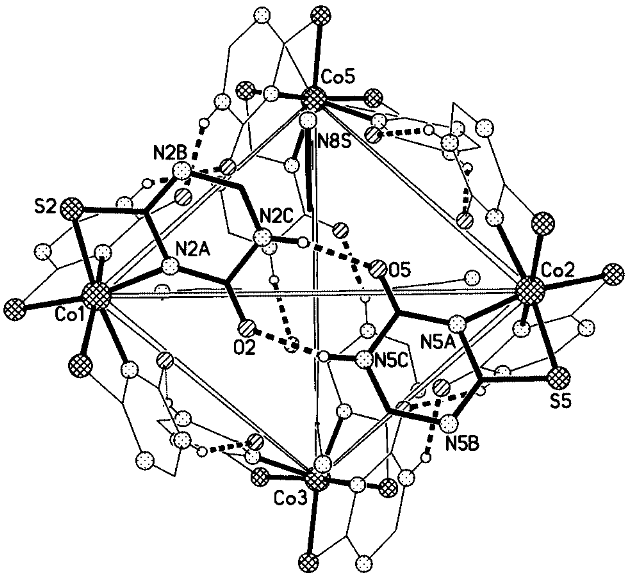


Fig. 8 One of two tetrahedral aggregates of molecules of compound **5** in the crystal. One pair of hydrogen-bonded OSta$^-$ ligands is shown in heavy lines for clarity. The Co · · · Co distances range from 9.78 to 9.95 Å. The O · · · N distances within the hydrogen-bonded pairs range from 2.743 to 2.945 Å. (The NEt$_2$ groups attached to the triazine rings have been omitted for clarity.)

tion mixture that gave **4** in very low yield. The structure (Fig. 7) contains a cobalt(III) site bound to the S- and N-donors of three chelating OStaH$^-$ ligands. The geometry is distorted octahedral, with the three sulfur and three nitrogen donor atoms in a *fac* arrangement. The bond lengths [Co–S 2.249–2.311(11), Co–N 1.84–1.98(3) Å] are the same as those for the Co(5) and Co(6) sites in **4**.

A curious feature of the structure of compound **5** is the presence of eight crystallographically independent molecules within the asymmetric unit. These eight molecules form two supramolecular tetrahedral aggregates, one of which is shown in Fig. 8. Four [Co(OStaH)$_3$] units lie with the Co at the vertices of a tetrahedron. The molecules are held together by pairs of hydrogen bonds between the N atom *para* to the S-donor and the exocyclic oxygen, *e.g.* N(2C)–O(5) and O(2)–N(5C) in Fig. 8. Four molecules of MeCN lie at the centres of the faces of the tetrahedral aggregate [*e.g.* N(8S) and attached C atoms in Fig. 8].

In both compounds **4** and **5** there is evidence for oxidation of Co^{II} to Co^{III}. We assume this oxidation has been caused by atmospheric oxygen, but have not yet been able to improve the yield of **4** or **5** by addition of oxidants or by bubbling dry O$_2$ through reactant or recrystallisation solutions.

Discussion

While the features required to stabilise metal complexes in solution are well understood, the requirements for forming stable complexes at the surfaces of metals, and hence modifying the properties of these metal surfaces, are less well studied. It was hoped that ligands based on derivatisation of cyanuric acid would offer the opportunity of varying the ligating properties of a series of ligands, changing from ligands that would strongly favour formation of stable solution complexes in a systematic fashion, to ligands which would bind strongly to surfaces.

While the cyanuric acid derivatives H$_2$S$_2$ta and H$_2$OSta can be synthesized straightforwardly, their reaction chemistry is more complex than anticipated. Two reactions, formation of disulfide bridges and nucleophilic displacement of one sulfur group by a thiolate from a second ligand, lead to oligomerisation of the ligands. These reactions produce unusual polydentate ligands *in situ*, but certainly rule out use of either H$_2$S$_2$ta or H$_2$OSta as a surface modifying ligand.

While neither the reaction to produce {(Sta)S(S$_2$ta)}$^{2-}$ nor that which gives {S(Ota)$_2$}$^{2-}$ is clean or high-yielding, and we have not yet isolated either ligand detached from the metal site, the results are intriguing. Both ligands are polydentate and polynucleating, and may have future applicability in synthesis of clusters, and possibly biomimetic chemistry; there is a great deal of interest in mixed N,S-donors for modelling active sites of metalloenzymes. However, there is a need to discover methods of controlling the formation of disulfides and condensation products before such studies are pursued. There is some evidence that the reactivity of the triazine derivatives can be controlled by choice of the group in the 4 position. While NEt$_2$ offered advantages in terms of ease of synthesis, it is possible that other side-chains would be preferable in producing more stable and malleable ligands.

The ligand OStaH$^-$ displays four bonding modes in compound **4**. In previous work we have frequently found pyridonate ligands show similarly flexible co-ordination chemistry. This creates some problems in describing the co-ordination mode in words, without recourse to diagrams. We find the currently approved notation, based on Greek letters μ and η, cumbersome. Recently, Harris at Edinburgh[17] has suggested an alternative notation, which we believe is markedly more intuitive and much simpler to use for ligands such as pyridonates. In Scheme 3 we have used the "Harris" notation to describe the bonding modes of OStaH$^-$ in **4**. The binding mode is referred to as $[X.Y_1Y_2Y_3 \ldots Y_n]$, where X is the overall number of metals bound by the whole ligand, and each value of Y refers to the number of metal atoms attached to the different donor atoms. Therefore for OStaH$^-$, which has three donor atoms [S, O and N(1)], the notation includes three values of Y. The ordering of Y is listed by the Cahn–Ingold–Prelog priority rules, hence here S before O before N.

An additional problem is presented by a ligand such as OStaH$^-$, where if the ligand is bound to more than one metal, and is chelating, it is difficult to indicate whether the N-donor is bound to the same metal as the sulfur or oxygen atom. While the chelating N,S mode is inherently more likely (and observed in compound **4**), there is still a need to distinguish between this and the N,O-chelating mode, which is not seen in **4**. To distinguish between these two alternatives we include a subscript number to show to which metal atom the donor is attached. So the mode $[2.1_11_21_1]$ would imply the N- and S-donors chelate to one metal and the O atom binds to the second, while $[2.1_11_21_2]$ would imply the N- and O-donors chelate and the S-donor binds to the second metal (see Scheme

3). A similar problem is presented if the ligand is trinucleating, and can be solved in a similar way.

Acknowledgements

We thank the EPSRC(UK) for funding for a diffractometer and for studentships (to S. G. H. and D. K. H). We also thank Dr Simon Coles (EPSRC Crystallographic Service, The University of Southampton) for collecting data on compound **4**.

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