The Preparation, X-Ray Crystal Structure and Theoretical Study of $[CoCp_2][S_3N_3]$, (Cp = Cyclopentadienyl), a Novel Stacking Compound Incorporating Multiple C–H···N(p_π) Interactions

Philip N. Jagg, Paul F. Kelly, Henry S. Rzepa, David J. Williams, J. Derek Woollins and William Wylie

Department of Chemistry, Imperial College of Science, Technology and Medicine, South Kensington, London SW7 2AY, UK

Reaction of cobaltocene, $[CoCp_2]$, with S_4N_4 in tetrahydrofuran (thf) results in precipitation of the cobaltocenium salt $[CoCp_2][S_3N_3]$ **1** in good yield; the X-ray crystal structure together with theoretical calculations reveal an accumulation of unique C–H···N···H–C (p_π) interactions that result in the formation of continuous stacks of alternating cations and anions.

The pseudo-aromatic S_3N_3 ring has been of great interest since it was first reported.[1] It can be prepared by reduction of S_4N_4 with reagents such as potassium, sodium sulphide and butyllithium.[2–4] However, the yields achieved in these reactions vary, as does the purity of the product. The redox properties of S_4N_4 have been investigated[5,6] and suggest that a relatively mild reducing agent should effect the transformation to $S_3N_3^-$. Here, we report on the reaction of cobaltocene, $[CoCp_2]$, with S_4N_4 to yield the salt $[CoCp_2][S_3N_3]$ **1**† [eqn. (1)] which has unusual and unexpected solid state stacking properties.

$$4[CoCp_2] + 3S_4N_4 \rightarrow \underset{\mathbf{1}}{4[CoCp_2][S_3N_3]} \qquad (1)$$

Complex **1** is insoluble in thf but dissolves in CH_2Cl_2 and, to a slight extent, water. It exhibits the expected bands due to the two ions in both the IR (ν_{max}/cm^{-1}: $[S_3N_3]^-$: 870vs and 453vs; $[CoCp_2]^+$ 641s) and UV (362 and 262 nm in MeCN) spectrum together with a ^1H NMR peak at δ 5.65 (CD_3CN) due to $[CoCp_2]^+$. Although these parameters confirm that **1** is a salt of $[S_3N_3]^-$, the colour of the solid compound (maroon red when powdered, almost black when crystalline) contrasts sharply with the yellow observed in solution, which is also the solid state colour of simple salts of either of the ions in **1**. To ascertain whether this colour was the result of cation–anion interactions an X-ray structure analysis was performed.‡

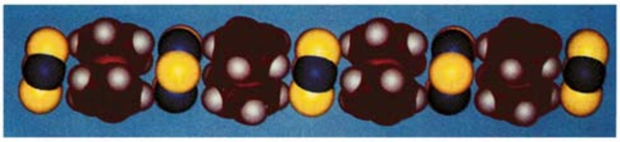

Fig. 1 Space filling representation of part of one of the infinite stacks of alternating $[CoCp_2]^+$ and $[S_3N_3]^-$ in the X-ray structure of **1**

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† In a typical reaction [eqn. (1)] a solution of $[CoCp_2]$ (0.203 g, 1.07 mmol) in thf (30 ml, thoroughly dried and degassed) was added to a stirred solution of S_4N_4 (0.148 g, 0.803 mmol) in an equal volume of thf. The mixture immediately darkened and produced a precipitate. After stirring for 1 h the dark-maroon coloured precipitate was filtered from the blue–purple solution and washed with thf (3 × 30 ml) and Et_2O (30 ml) then dried *in vacuo*. Yield 0.295 g, 84%. Recrystallisation from boiling MeCN afforded well formed dark red-black crystals suitable for X-ray analysis. Elemental analyses were satisfactory.

‡ *Crystal data* for **1**: $C_{10}H_{10}CoN_3S_3$, M = 327.3, monoclinic, a = 13.711(8), b = 10.213(6), c = 8.945(5) Å, β = 103.99(5)°, U = 1215 Å^3, space group $C2/c$, Z = 4 (the cobaltocenium cation is positioned about a centre of symmetry and the $[S_3N_3]^-$ anion about a twofold axis), D_c = 1.79 g cm^{-3}, μ(Cu-Kα) = 162 cm^{-1}. Data were measured on a Nicolet R3m diffractometer with graphite monochromated Cu-Kα radiation using ω-scans. The structure was solved by the direct methods and refined anisotropically using absorption-corrected data to give R = 0.025, R_w = 0.024 for 756 independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $2\theta \leq 116°$]. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

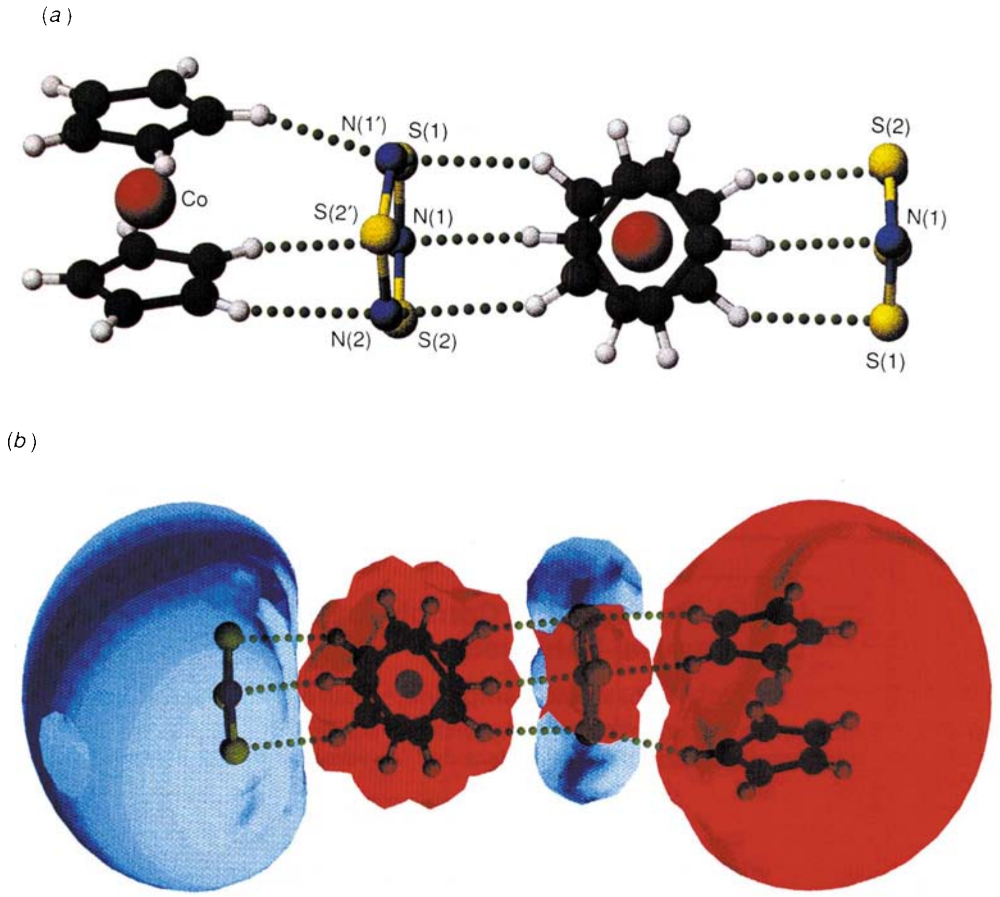

Fig. 2 (*a*) Part of the cation–anion stack of **1** in the crystal showing the C–H···N interactions; (*b*) the molecular electrostatic potential for the unit shown in (*a*), with the positive potential in red and the negative potential in blue

The $S_3N_3^-$ anion has crystallographic C_2 symmetry and near-planar geometry [the S(1)–N(1)–S(1′) and N(2)–S(2)–N(2′) planes are twisted by *ca.*4° with respect to each other about the C_2 axis]. All of the S–N bond lengths are equivalent, lying in the range 1.618(2)–1.625(2) Å. The angles at sulphur and nitrogen are in the ranges 116.1(1)–116.7(1) and 123.4(2)–123.7(2)° respectively. The cyclopentadienyl rings of the centrosymmetrical cobaltocenium cation are staggered (*ca.* 36° rotation) with their centroids 1.637 Å from the cobalt atom (*cf.* reported[7] mean value of 1.696 Å for Co–Cp).

The most striking feature of the structure is the packing of the cations and anions. These are arranged to form continuous stacks of alternating $[CoCp_2]^+$ cations and $[S_3N_3]^+$ anions, the Cp and S–N ring planes being orthogonal to each other (Fig. 1). The Cp C–H bonds are directed from both sides towards all three nitrogen atoms within each S–N ring. There are thus a total of six C–H···N interactions per anion. The geometry of each C–H···N···H–C arrangement is nearly linear with the angles subtended at nitrogen being 161° [N(1),N(1′)] and 175° [N(2)]. These observed distortions from linearity are a consequence of small mismatches in the relative dimensions of the cation and anion. The associated H···N, C···N distances and C–H···N angles are in the ranges 2.50–2.74 Å, 3.42–3.56 Å and 143–161° respectively. Although these distances would normally be considered to be too long for conventional hydrogen bonding the accumulation of six such interactions with the C–H groups pointing almost directly into the p_π orbitals of the nitrogen atoms undoubtedly determines the observed chain structure [Fig. 2(*a*)] with consequent (*i*) staggered geometry of the Cp rings; (*ii*) inversion of successive S–N rings with exchange of the S and N positions along the chain and (*iii*) the associated lateral displacement of 0.4 Å of the centroid of the S–N ring from the Co···Co axis. To our knowledge this is the first example of simultaneous p_π approach of two H atoms from opposite directions to a single N atom.§ This conclusion is further supported by comparison of the ν(CH) frequency in **1** with that in simple cobaltocenium salts[8] (**1**, 3068 cm^{-1}, $[CoCp_2]Br_3$ 3088 cm^{-1}, $[CoCp_2]Cl$ 3094 cm^{-1}). The directional nature of the π-facial hydrogen bonding in **1** is relatively unusual. Such aryl C–H···π-facial bonding has been observed in an organic system[11] but the π-plane to H distance was longer (2.7 Å) than we observe for **1**. Much shorter distances have been reported for O–H···π-facial interactions in 2,2,2-trifluoromethyl-1-(9-anthryl)-ethanol[12] where the highly directional nature of the bonding could be rationalised with the aid of calculated molecular electrostatic potentials.[13] Such a calculation is possible for **1** using the ZINDO/1 Hamiltonian[10] [Fig. 2(*b*)];¶ the results reveal that the attraction between the negative and positive regions is directed along the axis of the C–H bonds and the p_π orbitals.

The remaining C–H groups which are not used within the stack serve to bind adjacent stacks which are displaced laterally with the Cp rings adjacent to the edges of S_3N_3 rings (C···N 3.53 Å, H···N 2.60 Å, C–H···N 164°). Thus, the overall

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§ Hydrogen bonds of this type are rare though an example of a similar interaction involving an N–H(amide)···N(amide) where the bond is directed along the N(p_π) direction has been reported.[9]

¶ Calculations were performed using the atomic coordinates from the X-ray structure using a Tektronix CAChe workstation and the ZINDO Hamiltonian. Spectroscopic parameters for the cobalt atom[10] were employed, the MEP threshold was 0.05 a.u. with the resolution of 0.6 Å and a STO-3G basis set expansion.

geometry at nitrogen is approximately trigonal bipyramidal. An unusual feature of crystals of **1** is that the needle axis does not correspond to any of the crystallographic axes, although it is coincident with the cation–anion stacking direction. A simple conductivity measurement (pressed disc) indicates that **1** is an insulator. However, it is clear that slight modifications of either the cation or anion are likely to have significant effects and further work is underway.

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References

1 J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 1977, 453.

2 J. Bojes, T. Chivers, I. Drummond and G. Maclean, *Inorg. Chem.*, 1978, **17**, 3668.

3 J. Bojes and T. Chivers, *Inorg. Chem.*, 1978, **17**, 318.

4 R. Jones, P. F. Kelly, D. J. Williams and J. D. Woollins, *Polyhedron*, 1987, **6**, 1541.

5 T. Chivers and M. Hojo, *Inorg. Chem.*, 1984, **23**, 1526.

6 M. B. Hursthouse, M. Motevalli, P. F. Kelly and J. D. Woollins, *Polyhedron*, 1989, **8**, 997.

7 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.

8 D. Hartley and M. J. Ware, *J. Chem. Soc. (A)*, 1969, 138.

9 D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1977, 170.

10 W. P. Anderson, T. R. Cundari, R. S. Drago and M. C. Zerner, *Inorg. Chem.*, 1990, **29**, 1 and refs. cited therein.

11 T. A. Harmor, W. B. Jennings, L. D. Proctor, M. S. Tollen, D. R. Boyd and T. Mullen, *J. Chem. Soc., Perkin Trans. 2*, 1990, 25.

12 H. S. Rzepa, M. L. Webb, A. M. Z. Slawin and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 765.

13 F. J. Luque, F. Illas and M. Orozco, *J. Comput. Chem.*, 1990, **11**, 416.