The Occurrence of Both Amide and Thiolate Forms of the Benzoxazole-2-thionate Anion ($C_7H_4ONS^-$) in the Same Molecule: Synthesis and Crystal Structure of $C_7H_4ONSNa[\mu\text{-}OP(NMe_2)_3]_3NaC_7H_4ONS$†

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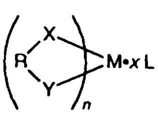
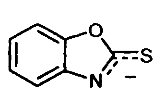
The reaction of benzoxazole-2(1*H*)-thione (C_7H_5ONS) with either solid NaOH or NaH, in toluene solution, in the presence of hexamethylphosphoramide (hmpa), afforded the new complex $C_7H_4ONSNa(\mu\text{-hmpa})_3NaC_7H_4ONS$ **1** in good yield. In contrast to similar lithium and calcium complexes, **1** resists the incorporation of water into the metal co-ordination sphere. Characterisation by single-crystal X-ray diffraction revealed that, in the solid state, complex **1** is dimeric through three bridging hmpa ligands. This dimer is unsymmetrically co-ordinated by $C_7H_4ONS^-$ anions, one metal centre being co-ordinated by a N,S-chelated anion formally derived from the thiol tautomer, the other being co-ordinated only through N of an anion formally derived from the amine tautomer of benzoxazole-2(1*H*)-thione. In addition to these unusual structural features, the dimeric complex **1** is further associated by weak C–H ··· O and C–H ··· S hydrogen bonding interactions.

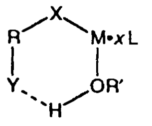
In recent years we have described a series of Group 1 and Group 2 metal chelate complexes of the type $(Y\text{–}R\text{–}X)_nM{\cdot}xL$, **A**, in which R is a heterocyclic framework, X and Y are electronegative centres, and L is a neutral ligand [*e.g.*, $O{=}P(NMe_2)_3$ (hmpa)].[1] Much of our work has focused on the benzoxazole-2-thionate ligand ($C_7H_4ONS^-$), which has been shown to chelate, through N and S, various metal centres including Li,[1c] Ca,[1d,1i] Sr[2] and Ba.[1d,1g] In addition, this versatile ligand has been shown capable of bonding to the early main-group metals through N whilst its displaced S atom interacts with either metal-bound protic donors such as water[1b,1c] and methanol[2b] *via* hydrogen bonding, **C**, or with salts of another metal (M′) such as Pt,[1e] Pd[2c] or Hg[1f] *via* a dative S–M′ interaction, **D** (where Z is an electronegative centre, *e.g.* Cl). In all the above cases analysis of bond lengths within $C_7H_4ONS^-$ shows that the negative charge is delocalised over both N and S. We report here on the synthesis and crystal structure of a sodium derivative of benzoxazole-2(1*H*)-thione, $C_7H_4ONSNa(\mu\text{-hmpa})_3NaC_7H_4ONS$, **1**, in which the two $C_7H_4ONS^-$ ligands within the molecular structure exhibit very different bonding behaviour to the metal centres, different both from all the cases described above, *and* from each other.



A; $n = 1$ or 2



B $C_7H_4ONS^-$



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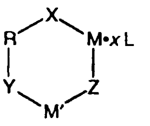

D

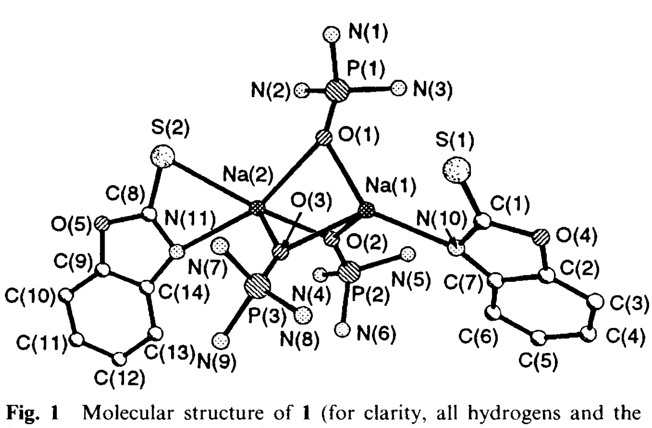

Fig. 1 Molecular structure of **1** (for clarity, all hydrogens and the hmpa methyl groups are omitted)

Results and Discussion

The synthesis of **1** has been achieved using either NaOH or NaH as the metal source. Initially, **1** was synthesised by adding a stoichiometric amount of solid NaOH to a toluene–hmpa solution of benzoxazole-2(1*H*)-thione. This is a proven route to aqua complexes of the type $(C_7H_4ONS)_nM^{n+}{\cdot}xL{\cdot}yH_2O$ (where M = Li, $n = 1$ or M = Ca, $n = 2$) by which the water is assembled *in situ*[1d] and it was the intention to synthesise such a complex where M = Na. Characterisation by ^1H NMR and IR spectroscopies, by elemental analysis, and finally by X-ray crystallography showed, however, that the product isolated was the anhydrous complex **1** and that the water produced by the reaction had not co-ordinated to the metal. Subsequently, **1** was also synthesised by reaction of solid NaH under similar conditions to the above, by which route only the anhydrous product could be obtained.

The molecular structure of **1**, obtained from the NaOH route, is shown in Fig. 1; selected bond lengths and angles, and fractional atomic coordinates are listed in Tables 1 and 2, respectively. The most immediate feature is the lack of water co-ordinated to the metal centres, in spite of its necessary presence in solution. This contrasts starkly with its lithium and calcium congeners. One possible explanation for these different behaviours is provided by *ab initio* molecular orbital (MO) calculations performed on $RM{\cdot}OH_2$ complexes, where R = cyclopentadienyl or H, and M = alkali metal.[3] They predict a

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

decrease in complexation energy of the order of 3.5 kcal mol^{-1} ($\approx$14.6 kJ mol^{-1}) on going from Li to Na which may be a significant enough reduction in stabilisation to preclude formation of an aqua complex for sodium. The M(μ-hmpa)$_3$M core is unusual but not unique; it has previously been observed in the inorganic complex (LiBr·1.5hmpa)$_2$[4] and in [Ph(NC$_5$H$_4$)NNa·1.5hmpa]$_2$ (NC$_5$H$_4$ = 2-pyridyl).[5] However, in **1** a more distinct pattern of bond lengths within the core is discernible; two hmpa ligands bridge with a marked asymmetry [Na(1)–O(1) 2.205(5), Na(2)–O(1) 2.603(5), Na(1)–O(2) 2.507(5), Na(2)–O(2) 2.208(4) Å], while the third bridges more symmetrically [Na(1)–O(3) 2.355(5), Na(2)–O(3) 2.243(4) Å]. Overall, however, both metals retain a near-identical Na–O environment [average Na(1)–O 2.360, average Na(2)–O 2.350 Å].

Further inspection of the structure of **1** reveals some very unusual features. First, the two $C_7H_4ONS^-$ ligands are *cisoid*. By analogy with structures of similar dimeric complexes, one would expect them to be *transoid*. Such is the case with all $C_7H_4ONS[M·hmpa]_2$ dimers {with the exception (C_7H_4ONS-Li·hmpa)$_2$·*o*-NH$_2$C$_6$H$_4$OH[1h] in which the $C_7H_4ONS^-$ ligands are necessarily *cisoid* in order to facilitate hydrogen bonding within the complex}, and in [Ph(NC$_5$H$_4$)NNa·1.5 hmpa]$_2$ whose similarity to **1** extends beyond the core of the structure to include bifunctional anions [N,N in this case rather than N,S as in **1**]. The second, and most remarkable, feature of the solid-state structure of **1** is the difference in the nature of the two anions attached to the sodium ions. The $C_7H_4ONS^-$ ligands are twisted such that a plane defined by one anion is at an angle of 27.7° to that defined by the other. In addition to, or maybe as a consequence of being twisted relative to each other, their bonding to sodium differs considerably, as revealed by inspection of the bond lengths involved [Fig. 2(*a*) and (*b*)]. For comparison, Fig. 2(*c*) and (*d*) show the bond lengths found in the crystal structures of the neutral benzoxazole-2(1*H*)-thione[6] and of a typical C_7H_4ONSLi complex [C_7H_4ONSLi·hmpa·MeOH]$_2$,[2b] respectively. Dealing first with the ligand bound to Na(1) [Fig. 2(*a*)], by consideration of Na–N and Na–S distances alone this ligand is formally derived from the amine tautomer of benzoxazole-2(1*H*)-thione rather than from the thiol tautomer [*i.e.*, from C(=S)–N(H) rather than C(–SH)=N]. The Na(1)–N(10) bond length of 2.361(5) Å is comparable to those found in other aromatic sodium amides {*cf.* shortest Na–N(amido) distances of 2.351(1) in (C$_4$Me$_4$NNa)$_\infty$ (2,3,4,5-tetramethyl-1-sodiopyrrole),[7] 2.478(5) and 2.236(5) Å in (C$_8$H$_6$NNa·tmen)$_2$ (*N*-sodioindole–tetramethylethylenediamine),[8] and 2.474(4) and 2.481(5) Å in (C$_8$H$_6$NNa·pmdien)$_2$ (pmdien = pentamethyldiethylenetriamine)[8]}. However, the comparison is not direct as no previous examples have involved a *terminally* bonded aromatic amide such as is seen here. Any bonding between S(1) and Na(1) is improbable on two counts. First, on the basis of distance alone: known Na–S bonds involving (formally) neutral S include 2.942(2) Å for a sulfur-containing macrocycle complex,[9] 2.895(2) Å in the inorganic complex [(NaNCS·hmpa)$_2$]$_\infty$,[10] and 2.749(2) to 2.927(2) Å for various Na–S interactions in a mixed Na–V thiolate complex.[11] In **1**, the Na(1)···S(1) distance is significantly longer, at 3.206(5) Å. Secondly, the bond lengths within this $C_7H_4ONS^-$ ligand show that it is indeed a

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

S(1)–C(1)	1.627(6)	C(1)–N(10)	1.376(7)
C(1)–O(4)	1.402(6)	N(10)–C(7)	1.324(6)
N(10)–Na(1)	2.361(5)	O(4)–C(2)	1.366(6)
S(2)–C(8)	1.772(6)	S(2)–Na(2)	2.777(4)
C(8)–N(11)	1.258(6)	C(8)–O(5)	1.471(6)
N(11)–C(14)	1.509(7)	N(11)–Na(2)	2.735(6)
O(5)–C(9)	1.408(6)	O(1)–Na(1)	2.205(5)
O(1)–Na(2)	2.603(5)	O(2)–Na(2)	2.208(4)
O(2)–Na(1)	2.507(5)	O(3)–Na(2)	2.243(4)
O(3)–Na(1)	2.355(5)		
N(10)–C(1)–O(4)	116.1(4)	N(10)–C(1)–S(1)	130.1(4)
C(1)–N(10)–Na(1)	105.0(3)	C(2)–O(4)–C(1)	99.2(4)
C(8)–S(2)–Na(2)	80.7(2)	N(11)–C(8)–O(5)	107.7(4)
N(11)–C(8)–S(2)	128.1(4)	C(8)–N(11)–C(14)	107.0(4)
C(8)–N(11)–Na(2)	91.7(3)	C(9)–O(5)–C(8)	111.4(4)
Na(1)–O(1)–Na(2)	79.41(12)	Na(2)–O(2)–Na(1)	81.50(14)
Na(2)–O(3)–Na(1)	84.29(12)		

Table 2 Atomic coordinates (× 10^4) for **1**

Atom	*x*	*y*	*z*
S(1)	12 500(1)	10 344(1)	3 403(1)
C(1)	12 748(4)	9 187(5)	3 944(3)
N(10)	12 343(3)	8 015(4)	3 900(2)
O(4)	13 502(3)	9 441(3)	4 541(2)
C(2)	13 556(4)	8 315(5)	4 858(3)
C(3)	14 225(4)	8 054(5)	5 443(3)
C(4)	14 149(4)	6 848(5)	5 637(3)
C(5)	13 455(5)	5 940(5)	5 253(3)
C(6)	12 794(4)	6 219(5)	4 669(3)
C(7)	12 844(4)	7 449(5)	4 469(3)
S(2)	8 029(1)	7 006(1)	500(1)
C(8)	7 245(4)	5 764(5)	899(3)
N(11)	7 432(3)	5 247(4)	1 510(2)
O(5)	6 218(3)	5 159(3)	552(2)
C(9)	5 756(4)	4 226(4)	1 007(3)
C(10)	4 726(4)	3 363(5)	917(3)
C(11)	4 476(4)	2 529(5)	1 466(3)
C(12)	5 174(4)	2 560(5)	2 077(3)
C(13)	6 192(4)	3 440(4)	2 149(3)
C(14)	6 487(4)	4 276(4)	1 600(3)
O(1)	11 195(3)	8 149(3)	1 612(2)
P	12 097(1)	8 110(1)	1 021(1)
N(1)	12 274(4)	9 410(4)	593(2)
C(15)	11 338(6)	10 241(6)	586(4)
C(16)	13 327(6)	9 779(6)	119(3)
N(2)	11 739(4)	7 021(4)	457(2)
C(17)	11 376(5)	7 193(6)	−275(3)
C(18)	11 436(6)	5 777(5)	722(3)
N(3)	13 457(4)	7 859(4)	1 317(2)
C(19)	14 324(5)	7 168(6)	951(3)
C(20)	14 018(5)	8 679(5)	1 858(3)
O(2)	10 667(3)	5 827(3)	2 523(2)
P(2)	10 888(1)	4 669(1)	2 874(1)
N(4)	10 551(3)	3 384(4)	2 453(2)
C(21)	9 264(5)	2 883(6)	2 345(3)
C(22)	11 392(5)	2 951(5)	1 931(3)
N(5)	12 364(4)	4 726(4)	3 037(3)
C(23)	12 870(6)	3 748(6)	3 403(4)
C(24)	13 291(5)	5 640(5)	2 723(4)
N(6)	10 019(4)	4 442(3)	3 592(2)
C(25)	9 936(7)	3 365(5)	4 035(4)
C(26)	9 591(5)	5 488(4)	3 952(3)
O(3)	8 992(3)	7 865(3)	2 814(2)
P(3)	8 045(1)	8 416(1)	3 236(1)
N(7)	7 601(4)	9 544(4)	2 762(2)
C(27)	6 655(5)	10 252(5)	3 036(3)
C(28)	7 739(5)	9 548(5)	1 995(3)
N(8)	8 417(3)	9 045(4)	3 996(2)
C(29)	8 613(5)	8 296(5)	4 619(3)
C(30)	9 080(5)	10 285(4)	4 036(3)
N(9)	6 928(3)	7 339(4)	3 480(2)
C(31)	5 863(5)	7 629(5)	3 905(3)
C(32)	6 642(5)	6 285(4)	3 027(3)
Na(2)	9 338(2)	6 732(2)	1 795(1)
Na(1)	11 130(2)	7 985(2)	2 833(1)

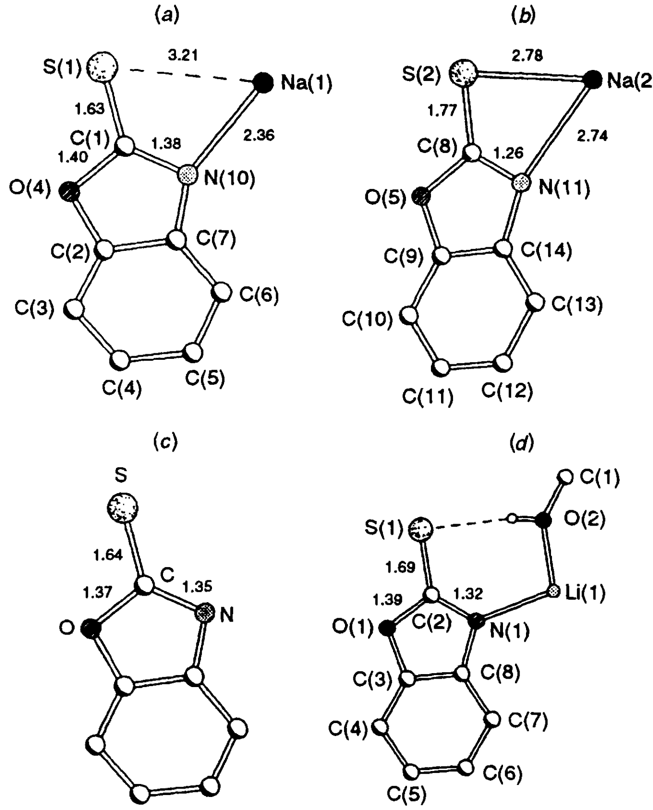
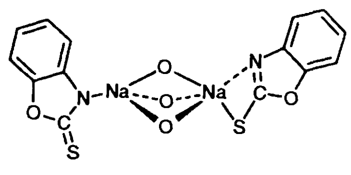


Fig. 2 Some bond lengths (Å) in $C_7H_4ONS^-$ ligands: (*a*) bound to Na(1) in **1**; (*b*) bound to Na(2) in **1**; (*c*) neutral C_7H_5ONS; (*d*) in $(C_7H_4ONSLi{\cdot}hmpa{\cdot}MeOH)_2$

terminally bonded aromatic amide, with no chelation from sulfur. The bond lengths C(1)–S(1) and C(1)–N(10) are 1.627(6) and 1.376(7) Å respectively [Fig. 2(*a*)] resembling closely the C=S and C–N distances found in the neutral thione [Fig. 2(*c*)] of 1.643(3) and 1.354(8) Å respectively. Were there a Na···S interaction, one would see a concomitant *lengthening* of C=S and *shortening* of C–N relative to the neutral (amine) ligand, brought about by delocalisation of the negative charge. Such is invariably found in cases where sulfur either chelates the metal, hydrogen bonds to a protic donor [Fig. 2(*d*)], or bonds to another metal. Turning to the ligand bound to Na(2) [Fig. 2(*b*)], bond lengths suggest that this is formally derived from the thiol tautomer of benzoxazole-2(1*H*)-thione. The bond length Na(2)–S(2) of 2.777(4) Å is shorter than the two found in $[2,4,6\text{-}(CF_3)_3C_6H_2SNa{\cdot}2thf]_\infty$ (thf = tetrahydrofuran),[12] of 2.838(2) and 2.835(2) Å, the only known aromatic sodium thiolate. The bond length Na(2)–N(11) of 2.735(6) Å is long but still consistent with interaction of a formally neutral, aromatic N with sodium {*cf.* the internal donor-sodium interactions seen in $[Me(NC_5H_4)NNa{\cdot}tmen]_2$[13] of 2.677(4) and 2.709(4) Å}. As before, the bond lengths within the ligand support these assertions. The expected slightly shortened C–S single bond and a slightly lengthened C=N double bond consistent with a thiolate that has a partially delocalised negative charge brought about by chelation of N to sodium are observed. The C(8)–S(2) bond length of 1.772(6) Å is far longer than the C=S double bond of the neutral thione, C_7H_5ONS, or of the anion attached to Na(1) [1.643(3) and 1.627(6) Å respectively] and is significantly longer than those found in typical $C_7H_4ONS^-M^+$ complexes where the delocalisation is greater [*cf.* Fig. 2(*d*) for example]. The C(8)–N(11) bond length of 1.258(6) Å is considerably shorter than the essentially single C–N bond of the ligand bound to Na(1) and that in neutral C_7H_5ONS, or the more delocalised bond common in C_7H_4ONSLi complexes [1.376(7) and 1.354(8), 1.32 Å]. The bonding pattern in **1** arrived at *via* the above arguments is summarised in Scheme 1.*



Scheme 1

The existence of two tautomeric forms of the same ligand in an early main group metal complex is not unprecedented but its occurrence normally has a clearly discernible foundation, *e.g.*, in the calcium complex $[(C_4H_3N_2OS)_2Ca{\cdot}2dmso{\cdot}H_2O]_2$ ($C_4H_4N_2OS$ = thiouracil, dmso = dimethyl sulfoxide)[15] the existence of two tautomers of the anion is directly attributable to a pattern of strong hydrogen bonding. In **1**, however, there are no such strong additional interactions. One might, for example, expect S(1) to be detached from Na(1) because of a strong hydrogen-bonding interaction, but in the absence of protic donors in **1** this is not a possibility. However, a point worthy of note is the existence of *weak* hydrogen bonding involving C–H hydrogen-bond donors. Molecular dimers of **1** are paired together by mutual O···H–C interactions involving the O atom of the $C_7H_4ONS^-$ ligand bound to Na(2) and a C–H bond of a C_6H_4 ring (estimated O···H 2.507, O···C 3.281 Å). Although distance is a relatively insensitive criterion for such a weak [typically 1–2 kcal mol^{-1} (≈4.2–8.4 kJ mol^{-1})] and electrostatic interaction, the distance here falls well within the range of 3.0–4.0 Å in which such hydrogen bonds are considered possible.[16] In addition to this O···H–C bonding, these pairs of dimers are further associated by means of mutual S···H–C interactions between an hmpa hydrogen belonging to another pair of dimers and sulfur [S(2)] of $C_7H_4ONS^-$ (estimated S···H distance 2.911, C···S distance 3.809 Å), thereby propagating an infinite chain of hydrogen-bonded molecules (Fig. 3). It should be stressed that these interactions offer no obvious explanation of the observation of two $C_7H_4ONS^-$ tautomers within the dimeric structure. They do, however, highlight a type of intermolecular interaction the significance of which has only recently been understood in explaining hydrogen-bonding patterns and crystal packing in organic molecules[17] and the existence of which in the solid-state structures of *metallated* organic molecules has been, as yet, largely unobserved or ignored.

Experimental

General Procedures and Materials.—All reactions were carried out using freshly distilled solvents under an atmosphere of nitrogen gas using standard inert-atmosphere techniques. Isolated products were handled under an argon atmosphere in a glove box. Proton NMR spectra were recorded using a Bruker WM250 spectrometer. Samples for elemental analysis were sealed in aluminium boats under argon gas in a glove box prior to analysis using a Perkin-Elmer 240 elemental analyser. All starting materials were purchased from Aldrich. Hexamethylphosphoramide was dried over molecular sieve (13X), other starting materials were used without further purification.

*Reaction of Benzoxazole-*2(1H)*-thione with* NaOH.—Toluene (10 cm^3) was added to NaOH (5 mmol, 0.20 g) and benzoxazole-2(1*H*)-thione (5 mmol, 0.76 g) in a nitrogen-filled Schlenk tube. Addition of hmpa (7.5 mmol (1.40 cm^3) and stirring at room temperature for 2 h resulted in the precipitation of a

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* In a superficially similar structure, where the anion differs from that in **1** only in having a heterocyclic sulfur atom (rather than oxygen), the dimer adopts the expected *transoid* configuration and both ligands bind sodium as amide anions.[14]

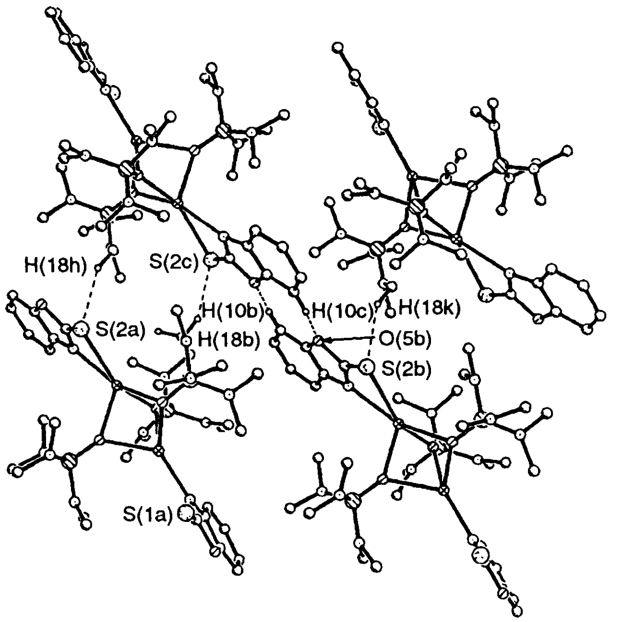

Fig. 3 Intermolecular C–H···O and C–H···S hydrogen bonding in **1**

cream coloured powder, and then warming caused dissolution to give a golden brown solution. Cooling to room temperature and standing for 24 h resulted in a crop of golden cubic crystals of **1** (2.83 g, 64%), m.p. 110–112 °C [Found (Calc.): C, 43.3 (43.5); H, 7.1 (7.0); N, 16.6 (17.4)%]. ^{1}H NMR (250 MHz, [$^2H_6$]dmso, SiMe$_4$, 25 °C): δ 2.53 (d, 27 H, hmpa), 6.86–7.31 [m, 4 H, $C_7H_4ONS^-$].

*Reaction of Benzoxazole-*2(1H)*-thione with* NaH.—Synthesis of **1** using NaH as the metal source was similar to the procedure above except that the solution was stirred at 70 °C in an oil bath for 2 h, resulting in vigorous gas evolution and slow dissolution of the hydride into a golden brown solution.

Crystal Structure Determination of Compound **1**.—A golden brown crystal of **1** (approximate dimensions 0.30 × 0.20 × 0.15 mm) was removed directly from solution under a stream of argon gas and coated in an inert, perfluorinated oil (Riedel-de Haën RS 3000) prior to mounting on a glass fibre and immediate transfer to the diffractometer.

Crystal data. $C_{32}H_{62}N_{11}Na_2O_5P_3S_2$, M_r = 883.94, triclinic, space group $P\bar{1}$, a = 10.98(2), b = 11.02(2), c = 18.00(3) Å, α = 89.90(3), β = 88.77(3), γ = 89.09(3)°, U = 2178(7) Å^3 (from least-squares refinement of the 2θ values of 52 reflections; $20 < 2\theta < 25°$), Z = 2, ρ_{calc} = 1.348 Mg m^{-3}, $F(000)$ = 940, λ(Mo-Kα) = 0.710 73 Å, μ(Mo-Kα) = 0.304 mm^{-1}, T = 120(2) K.

Data collection and processing. Data were collected on a Stoe-Siemens four-circle diffractometer at 120 K, ω–2θ scan mode with graphite-monochromated Mo-Kα radiation. Diffraction data were measured to a maximum θ value of 24°. Three standard reflections were monitored every 90 min and showed a 5% decrease in standard intensity over the time of the data collection. A total of 7134 reflections were measured within the ranges $-11 < h \leqslant 11$, $-11 < k \leqslant 11$, $-17 < l \leqslant 20$ and averaged to yield 5865 unique reflections (R_{int} = 0.0929) of which 4200 were judged significant by the criterion that $I > 2\sigma(I)$.

Structure analysis and refinement. The structure was solved by direct methods[18] and refinement, based on F^2, was by full-matrix least-squares techniques.[19] All non-hydrogen atoms were refined anisotropically, hydrogens were placed in calculated positions (C–H 0.95 and 0.98 Å for aromatic and methyl hydrogens) and refined using a riding model. Refinement for 5858 data (18 restraints and 516 parameters) converged to $wR2$ = 0.1456 (all data), $R1$ = 0.0591 (observed data), goodness-of-fit = 1.036, weighting scheme $w = 1/[\sigma^2(F_o^2) + (0.1087P)^2 + 2.1651P)]$, where $P = (F_o^2 + 2F_c^2)/3$, σ obtained from counting statistics. A final electron density Fourier-difference synthesis revealed maximum and minimum residual electron density peaks of 0.53 and −0.51 e Å^{-3}, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 (*a*) D. R. Armstrong, R. E. Mulvey, D. Barr, R. W. Porter, P. R. Raithby, T. R. E. Simpson, R. Snaith, D. S. Wright, K. Gregory and P. Mikulcik, *J. Chem. Soc., Dalton Trans.*, 1991, 765; (*b*) D. Barr, P. R. Raithby, P. v. R. Schleyer, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1990, 643; (*c*) D. R. Armstrong, D. Barr, P. R. Raithby, P. v. R. Schleyer, R. Snaith and D. S. Wright, *Inorg. Chim. Acta*, 1991, **185**, 163; (*d*) P. Mikulcik, P. R. Raithby, R. Snaith and D. S. Wright, *Angew. Chem.*, 1991, **103**, 452; *Angew. Chem., Int. Ed. Engl.*, 1991 **30**, 428; (*e*) M. G. Davidson, P. R. Raithby, R. Snaith, D. Stalke and D. S. Wright, *Angew. Chem.*, 1991, **103**, 1696; *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1648; (*f*) M. G. Davidson, S. C. Llewellyn, M.-I. Lopez Solera, P. R. Raithby, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1992, 573; (*g*) F. A. Banbury, M. G. Davidson, A Martin, P. R. Raithby, R. Snaith, K. L. Verhorevoort and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1992, 1152; (*h*) D. R. Armstrong, F. A. Banbury, M. G. Davidson, P. R. Raithby, R. Snaith and D. Stalke, *J. Chem. Soc., Chem. Commun.*, 1992, 1492; (*i*) M. G. Davidson, M. Gerloch, S. C. Llewellyn, P. R. Raithby and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1993, 1363.

2 M. G. Davidson, Ph.D. Thesis, University of Cambridge, 1994.

3 C. Lambert and P. v. R. Schleyer, *Methoden der Organische Chemie* (*Hoüben-Weyl*), Thieme-Verlag, Stüttgart, 1993, vol. E19d, pp. 1–98.

4 D. Barr, M. J. Doyle, R. E. Mulvey, P. R. Raithby, D. Reed, R. Snaith and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1989, 318.

5 P. C. Andrews, W. Clegg and R. E. Mulvey, *Angew. Chem.*, 1990, **102**, 1480; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1440.

6 P. Groth, *Acta Chem. Scand.*, 1973, **27**, 945.

7 N. Kuhn, G. Henkel and J. Kreutzberg, *Angew. Chem.*, 1990, **102**, 1179; *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1143.

8 K. Gregory, M. Bremer, W. Bauer and P. v. R. Schleyer, *Organometallics*, 1990, **9**, 1485.

9 F. Teixidor, C. Viñas, J. Rius, C. Miravitlles and J. Casabó, *Inorg. Chem.*, 1990, **29**, 149.

10 D. Barr, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith and D. S. Wright, *Polyhedron*, 1989, **8**, 215.

11 J. K. Money, J. C. Huffman and G. Christou, *Inorg. Chem.*, 1988, **27**, 507.

12 S. Brooker, F. T. Edelmann, T. Kottke, H. W. Roesky, G. M. Sheldrick, D. Stalke and K. H. Whitmire, *J. Chem. Soc., Chem. Commun.*, 1991, 144.

13 P. C. Andrews, D. R. Baker, R. E. Mulvey, W. Clegg and P. O'Neil, *Polyhedron*, 1991, **10**, 1839.

14 P. C. Andrews, personal communication.

15 F. A. Banbury, M. G. Davidson, A. J. Edwards, M.-I. Lopez Solera, P. R. Raithby, R. Snaith, D. Stalke and D. S. Wright, *Inorg. Chim. Acta*, 1993, **203**, 93.

16 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.

17 See, for example, G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290; C. B. Aakerröy and K. R. Sneddon, *Chem. Soc. Rev.*, 1993, **21**, 397.

18 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.

19 G. M. Sheldrick, SHELXL 93, Program for crystal structure refinement, University of Göttingen, 1993.

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