Two Monomeric, Octahedral Complexes of Alkaline Earth Metal Salts: Syntheses,† Physical Characteristics, and Crystal Structures of $SrI_2{\cdot}4HMPA$ and $Sr(NCS)_2{\cdot}4HMPA$ [HMPA = $O:P(NMe_2)_3$]

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The complexes $(SrI_2{\cdot}4HMPA)_n$, (**1**), and $[Sr(NCS)_2{\cdot}4HMPA]_n$, (**2**), [HMPA = $O:P(NMe_2)_3$], were synthesised by reactions of Sr metal, NH_4X solids (X = I and SCN, respectively), and HMPA (1 : 2 : 4 molar amounts) in toluene, and several HMPA complexes of calcium and barium halide and thiocyanate salts have been made by analogous routes; *X*-ray diffraction has shown that both Sr species have discrete molecular ($n = 1$), octahedral structures, the X groups being *trans* in (**1**) but *cis* in (**2**).

We have recently reported[1] a novel route to simple complexes of alkali metal salts, $(MX{\cdot}xL)_n$ [M = Li, Na, K; X = halogen, SCN; L = hexamethylphosphoramide (HMPA), tetramethylethylenediamine (TMEDA)] by reacting solid ammonium salts, NH_4X, with metal sources (Bu^nLi solution, MH or M solids) in toluene containing stoicheiometric amounts of Lewis base donor, L. Such an '*in situ*' route has two distinct advantages over a direct one. First, attempted direct dissolution of supposedly anhydrous $(MX)_\infty$ salts in L often produces complexes containing variable amounts of H_2O since the precursor salts themselves are very prone to pre-hydration;[1a,2] in contrast, ammonium salts are not in general hygroscopic. Second, such attempted dissolution of the extant infinite lattice often fails; again in contrast, an infinite 3-d lattice is never allowed to form in the *in situ* method, which presumably involves initial generation of MX monomers whose association, under the conditions involved, is limited/prevented by the presence of the small donor molecules, L. In principle, this route is applicable to many other electropositive metals and, as a further advantage, it could provide new discrete, oligomeric molecular materials, with properties reminiscent of covalently bonded species yet, by definition almost, ones containing still highly ionic bonds. Here we describe the first such extension of the route, to complexes of alkaline earth metal salts, *viz*, to $(SrI_2{\cdot}4HMPA)_n$, (**1**), and to $[Sr(NCS)_2{\cdot}4HMPA]_n$, (**2**) [HMPA = $O:P(NMe_2)_3$]. *X*-ray diffraction studies have shown that both complexes are monomers ($n = 1$), with octahedral arrangements about their central Sr^{2+} ions. In (**1**), the I^- ligands are *trans* while in (**2**) the SCN^- ligands are *cis*.

A mixture of NH_4I solid (1.45 g, 10 mmol), Sr solid (0.44 g, 5 mmol), and HMPA (3.58 g, 20 mmol) in toluene (12 ml) was refluxed for ~1 h; the solids reacted gradually and dissolved, giving finally a clear colourless solution. Cooling gave a large crop (86% yield) of colourless crystals, identified as $(SrI_2{\cdot}4HMPA)_n$, **1**.‡ A similar reaction, substituting NH_4SCN for NH_4I, gave colourless crystals of $[Sr(NCS)_2{\cdot}4HMPA]_n$, (**2**),‡ in 77% first batch yield. Attempts to obtain (**1**) or a related HMPA-complex by direct methods failed. Firstly, the hydrate $SrI_2{\cdot}6H_2O$ shows no significant dissolution in neat HMPA even at the reflux temperature. Secondly, although the hexahydrate affords mixed $SrI_2{\cdot}xH_2O$ ($x = \frac{1}{2}$, 1, 2) solids at 150 °C, total dehydration proves impossible, even at 450 °C (where there is substantial decomposition, producing iodine).

Although the central bonding within (**1**) and (**2**) must be highly electrostatic in nature [both Sr–I and Sr–N (of NCS), and Sr–O (of HMPA) bonds], their simple properties presaged discrete molecular structures. Both complexes have relatively low melting points {193—196 °C for (**1**), *cf.* 515 °C for $(SrI_2)_\infty$;[3] 174—175 °C for (**2**), *cf* $[Sr(SCN)_2]_\infty$ 160—170 °C decomp.[3]} and exhibit high solubilities in arenes (*e.g.*, >2

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† The ammonium salt route to complexes of metal salts is being patented by the Associated Octel Co. Ltd., U.K. (European Patent Application Number 88309913.7).

‡ Satisfactory elemental analyses (C, H, N; I; P; Sr) were obtained for (**1**) and (**2**).

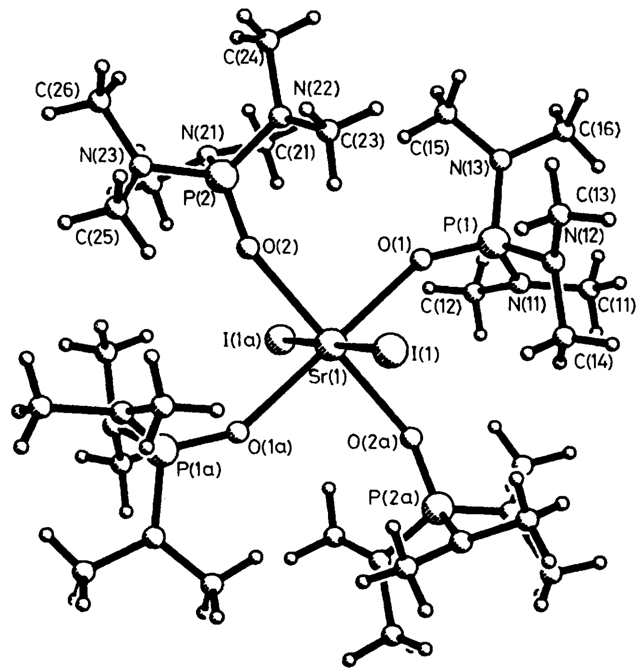

Figure 1. Molecular structure of SrI_2·4HMPA (**1**) showing the atom numbering scheme.§

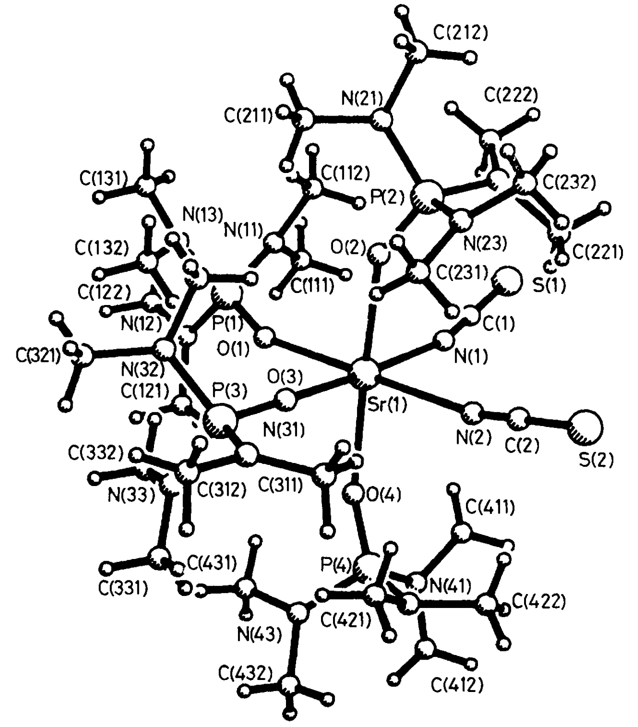

Figure 2. Molecular structure of $Sr(NCS)_2$·4HMPA (**2**) showing the atom numbering scheme.§

g/ml of benzene). These indications have been verified by *X*-ray diffraction studies which have revealed monomeric (n = 1) octahedral structures [(**1**), Figure 1; (**2**), Figure 2]. Complex (**1**) contains a linear I–Sr–I axial unit [Sr–I distance, 3.321(1) Å; I–Sr–I, 180.0(1)°] and four equatorial Sr–O contacts [Sr–O(1), (1a) 2.450(4) Å, Sr–O(2), (2a) 2.430(3) Å]. In complex (**2**), however, the anionic ligands are *cis* [mean Sr–N (of NCS) distance, 2.596 Å; N(1)–Sr–N(2), 93.4(2)°; N(1)–Sr–O(3), 175.8(2)°; N(2)–Sr–O(1), 177.0(2)°]. There are no significant intermolecular contacts in the solid-state structures of (**1**) and (**2**), a fact reflected in their low melting points and high arene solubilities.

Perhaps surprisingly (in view of their simplicity), (**1**) and (**2**) represent a totally new structural class for heavier alkaline earth metal (Sr, Ba) complexes. Six-co-ordination of these metals is unusual, if not unprecedented (no such examples were found in a search of the Cambridge crystallographic data base[4]); it occurs but rarely for calcium salt complexes, *e.g.*, for $CaCl_2·4H_2O$ (trigonal prismatic) and for $CaBr_2·4MeOH$ (distorted octahedral).[5] For strontium in particular (though also for barium) co-ordination numbers of 7—9 or above are the norm. These occur (i) in polyhedra connected by inter-unit anion · · · M^{2+} contacts, *e.g.*, $MX_2·H_2O$ (M = Sr, Ba; X = Cl, Br, I) consist of face-sharing $MX_7·(H_2O)_2$ tricapped trigonal prisms,[6] (ii) in discrete species with multidentate open-chain ether ligands, *e.g.*, $Sr(SCN)_2·xH_2O$ (x = 1 or 2) complexes with glymes (tri-, tetra-, penta-, hexa-), which retain SCN^- · · · Sr^{2+} contacts,[7] (iii) in crown complexes, which frequently separate metal cation and anion(s),[5] *e.g.*, $[Sr(\text{benzo-18-crown-6})·3H_2O]·(ClO_4)_2$.[8] It is noticeable that the Sr–I distances in (**1**) are, relatively, rather short, *cf.* average values of 3.351 Å in $(SrI_2)_\infty$ (seven-co-ordinate around Sr^{2+}),[9] 3.500 Å in $SrI_2·H_2O$,[6] 3.491 Å in $SrI_2·2H_2O$ (nine-co-ordinate around Sr^{2+}).[10] The Sr–O distances in (**1**) and (**2**) are, relatively, yet markedly shorter: average Sr–O distances in the aquo and glyme complexes of SrI_2 and $Sr(SCN)_2$ cited above range from 2.584—2.732 Å [*cf.* a mean of 2.440 Å in (**1**), 2.444 Å in (**2**)]. It may be that HMPA is an especially good donor to Sr^{2+}, thus stabilising (**1**) and (**2**) as discrete molecular species retaining metal–anion bonds, though we prefer to believe that these geometric features are symptomatic of the synthetic method used, *i.e.*, interception of an $M^{II}X_2$ (or M^IX^1) unit by donors present.

Apart from (**1**) and (**2**), the NH_4X/M^{II} route in HMPA/toluene has already provided numerous complexes of type $MX_2·x$HMPA (M = Ca; X = Cl, x = 3; X = Br, I, x = 4; X = NCS, x = 2 or 4/M = Sr; X = Cl, x = 3; X = Br, x = 4; X = NCS, x = 2/M = Ba; X = Br, x = 4; X = I, x = 3 or 4; X = NCS, x = 2 or 4). Yields are usually 75% + and m.pts. are low, ranging from 72 °C [for $Ba(SCN)_2·2HMPA$] to 220 °C (for

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§ *Crystal data*: (**1**), $C_{24}H_{72}I_2N_{12}O_4P_4Sr$, M = 1058.2, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), a = 12.361(3), b = 14.456(4), c = 12.985(4) Å, β = 107.86(2)°, U = 2209(1) Å^3, Z = 2, D_c = 1.591 g cm^{-3}, $F(000)$ = 1072, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, $\mu(\text{Mo-}K_\alpha)$ = 27.51 cm^{-1}. 3406 Reflections collected on a Stoe–Siemens four-circle diffractometer in the range $5 < 2\theta < 45°$. The structure was solved by a combination of Patterson and Fourier difference techniques, and refined by full matrix least squares (all non-hydrogen atoms anisotropic) to R = 0.033, R_w = 0.047 $\{w^{-1} = \sigma^2(F) + 0.0008F^2\}$, for 2614 unique reflections $[F > 4\sigma(F)]$. (**2**), $C_{26}H_{72}N_{14}O_4P_4S_2Sr$, M = 920.6, monoclinic, space group $P2_1/n$ (non-standard setting of $P2_1/c$, No. 14), a = 12.872(3), b = 20.992(5), c = 18.006(5) Å, β = 97.09(2)°, U = 4828(2) Å^3, Z = 4, D_c = 1.266 g cm^{-3}, $F(000)$ = 1952, $\lambda(\text{Mo-}K_\alpha)$ = 0.71073 Å, $\mu(\text{Mo-}K_\alpha)$ = 13.38 cm^{-1}. 6967 Reflections collected on a Nicolet *R3m/V* four-circle diffractometer in the range $5 < 2\theta < 45°$. The structure was solved by a combination of Patterson and Fourier difference techniques, and refined by full matrix least squares (all non-hydrogen atoms anisotropic) to R = 0.065, R_w = 0.066 $\{w^{-1} = \sigma^2(F) + 0.0005F^2\}$, for 4008 unique reflections $[F > 4\sigma(F)]$. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crytallographic Data Centre. See Notice to Authors Issue No. 1.

$CaBr_2 \cdot 4HMPA$). The materials also show good (~1 g/ml) to extreme (~3 g/ml) solubility in arene solvents, and we are finding that the soluble halides are convenient precursors to organometallics of general formulae $RMX \cdot x HMPA$ and $R_2M \cdot x HMPA$ (M = Ca, Sr, Ba; X = Cl, Br, I) *via* their reactions with organolithiums, RLi.

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References

1 (a) D. Barr, R. Snaith, D. S. Wright, R. E. Mulvey, and K. Wade, *J. Am. Chem. Soc.*, 1987, **109**, 7891; (b) D. Barr, M. J. Doyle, R. E. Mulvey, P. R. Raithby, R. Snaith, and D. S. Wright, *J. Chem. Soc., Chem. Commun.*, 1988, 145; (c) D. Barr, M. J. Doyle, S. R. Drake, P. R. Raithby, R. Snaith, and D. S. Wright, *ibid.*, 1988, 1415; (d) D. Barr, M. J. Doyle, P. R. Raithby, R. Snaith, D. S. Wright, R. E. Mulvey, and D. Reed, *ibid.*, 1989, 318.

2 C. L. Raston, B. W. Skelton, C. R. Whitaker, and A. H. White, *Aust. J. Chem.*, 1988, **41**, 409; C. L. Raston, C. R. Whitaker, and A. H. White, *ibid.*, 1988, **41**, 413.

3 'Handbook of Chemistry and Physics,' ed. R. C. Weast, 69th edn. 1988—1989, C.R.C. Press Inc., Florida, U.S.A.

4 Cambridge Crystallographic Data Base; Director: Dr. O. Kennard, University of Cambridge.

5 N. S. Poonia and A. V. Bajaj, *Chem. Rev.*, 1979, **79**, 389 and references therein.

6 H. D. Lutz, W. Buchmeier, and B. Engelen, *Acta Crystallogr., Sect. B*, 1987, **43**, 71.

7 Y. Y. Wei, B. Tinant, J-P. Declercq, M. van Meerssche, and J. Dale, *Acta Crystallogr., Sect. C*, 1987, **43**, 1076; 1080; 1270; 1274.

8 D. L. Hughes, C. L. Mortimer, and M. R. Truter, *Inorg. Chim. Acta*, 1978, **29**, 43.

9 E. Th. Rietschel and H. Bärnighausen, *Z. Anorg. Allg. Chem.*, 1969, **368**, 62.

10 W. Buchmeier and H. D. Lutz, *Acta Crystallogr., Sect. C*, 1986, **42**, 651.