Notes

Reactions of $(NSCl)_3$ with Lewis Acids and Sulphur: a Convenient Preparation of $[S_2N][SbCl_6]$

Arthur J. Banister and Aidan G. Kendrick
Department of Chemistry, University of Durham Science Laboratories, South Road, Durham DH1 3LE

Reaction of $(NSCl)_3$ with $SbCl_5$ in thionyl chloride or methylene chloride, in molar ratio 1:3, followed by the addition of three equivalents of elemental sulphur produces $[S_2N][SbCl_6]$, $[S_3N_2Cl][SbCl_6]$, and $[NS_2Cl_2][SbCl_6]$; the adduct $S_4N_4{\cdot}SbCl_5$ was also produced in methylene chloride. The products can be separated by solvent extraction; the overall yield of $[S_2N][SbCl_6]$ is 35%. A similar reaction in methylene chloride using $FeCl_3$ instead of $SbCl_5$ produced $[S_6N_4][FeCl_4]_2$.

Reactions of Lewis acids with $(NSCl)_3$ have been extensively studied.[1] The products isolated depend on reaction conditions and molar ratios of reactants. The intermediate precipitates formed in these reactions, although not separately characterised, have been used as *in situ* sources of the reactive SN^+ cation, *e.g.* for the synthesis of $S_5N_5^+$ and $NS_2Cl_2^+$ salts: equations (1) (M = Fe[2] or Al[2]) and (2) (M = Fe,[3] Al,[3] or B[4]) respectively. The compound $[NS_2Cl_2][SbCl_6]$ has also been prepared[3] *via* equation (2). The synthesis of $[S_5N_5][AsF_6]$ and $[NS_2Cl_2][AsF_6]$, from reactions of $[SN][AsF_6]$ with S_4N_4 and SCl_2 respectively,[5] provided evidence that (for strong Lewis acid halides) the intermediate ('$NSCl{\cdot}MCl_3$') was probably SN^+-MCl_4^- rather than an adduct, *e.g.* $ClSN \rightarrow MCl_3$, especially since the reaction of $[SN][SbCl_6]$[6] or $[SN][AsF_6]$[7,8] with elemental sulphur has been found to yield S_2N^+ salts; in the case of $[SN][AsF_6]$, the reaction is quantitative.[8]

$$(NSCl)_3 + 3MCl_3 \xrightarrow{SOCl_2} 3NSCl{\cdot}MCl_3 \xrightarrow{3S_4N_4} 3[S_5N_5][MCl_4] \quad (1)$$

$$(NSCl)_3 + 3MCl_3 \xrightarrow{SOCl_2} 3NSCl{\cdot}MCl_3 \xrightarrow{3SCl_2} 3[NS_2Cl_2][MCl_4] \quad (2)$$

We were interested in extending this synthetic principle to obtain a more convenient preparation of an S_2N^+ salt. It has been shown that S_2N^+ has an extensive and diverse chemistry[9,10] and is of increasing use as a 'building block' in synthesis of sulphur–nitrogen compounds. We attempted the preparation of $[S_2N][SbCl_6]$ by reacting elemental sulphur with the precipitate formed on addition of $SbCl_5$ to $(NSCl)_3$. To assess the effect of using a weaker Lewis acid, the reaction was repeated using $FeCl_3$ in place of $SbCl_5$.

Results and Discussion

Reaction of $(NSCl)_3$, $SbCl_5$, *and Sulphur* (1:3:3).—The products isolated from this reaction and identified by i.r. spectroscopy were $[S_2N][SbCl_6]$, $[S_3N_2Cl][SbCl_6]$, and $[NS_2Cl_2][SbCl_6]$; in CH_2Cl_2 the adduct $S_4N_4{\cdot}SbCl_5$ was also formed. The co-products were easily separated from $[S_2N][SbCl_6]$ by extraction with SO_2; $[S_2N][SbCl_6]$, isolated in *ca.* 30% yield, was further characterised by Raman spectroscopy and elemental analysis (S, N, Cl, and Sb).

Different solvents and reaction conditions were used in an attempt to maximise the yield of $[S_2N][SbCl_6]$. It was found that CH_2Cl_2 or $SOCl_2$ were suitable solvents and that, in general, higher yields of $[S_2N][SbCl_6]$ were obtained using higher reaction temperatures or longer reaction times; low-temperature ractions (0 to −5 °C) resulted in greatly reduced yields. An attempt to prepare $[S_2N][SbCl_6]$ in nitromethane was only partially successful; removal of solvent from the intensely coloured reaction mixture yielded a red tar, from which $[S_2N][SbCl_6]$ could not be readily isolated. Infrared spectroscopy indicated considerable protonation at nitrogen, presumably arising from the proton acidity of the solvent. The formation of red tars on evaporation of CH_3NO_2 solutions containing sulphur–nitrogen cations has been encountered previously.[8]

The major co-products isolated from the reactions in CH_2Cl_2 or $SOCl_2$, *viz.* $[S_3N_2Cl][SbCl_6]$ and $[NS_2Cl_2][SbCl_6]$, probably formed (respectively) by cycloaddition of $[S_2N][SbCl_6]$ to NSCl units, and as a result of chlorination[11] of $[S_2N][SbCl_6]$ [by $(NSCl)_3$, $SbCl_5$, or $SOCl_2$]. The adduct $S_4N_4{\cdot}SbCl_5$[12] probably arose from formation of traces of S_4N_4 by dechlorination of $(NSCl)_3$ (*e.g.* by S_2N^+) followed by reaction with $SbCl_5$; the adduct is not formed in the mildly chlorinating solvent, $SOCl_2$. The formation of these co-products is not a serious problem in the preparation of $[S_2N][SbCl_6]$ owing to the ease of separation (solvent extraction by SO_2, in which it is insoluble).

$[S_2N][SbCl_6]$ was first prepared in unspecified yield by the reaction of S_7NH, S_7NBCl_2, or 5,8-$S_6(NH)_2$ with $SbCl_5$ in liquid SO_2[13] and $[S_2N][AlCl_4]$ has been isolated in unspecified yield from the reaction between S_4N_4 and $AlCl_3$ in methylene chloride.[14] Later work[9] showed that $[S_2N][AsF_6]$ can be prepared according to equations (3) and (4) in liquid SO_2. The yields were 20 and 77% respectively; in the absence of traces of bromine, the yield for reaction (4) was only *ca.* 30%. Very recently,[8] reaction (5) has been used to prepare $[S_2N][AsF_6]$ in almost quantitative yield, but this route has the disadvantage of requiring the prior preparation and isolation of $[SN][AsF_6]$

$$[S_8][AsF_6]_2 + NaN_3 \longrightarrow [S_2N][AsF_6] + NaAsF_6 + N_2 + \tfrac{3}{4}S_8 \quad (3)$$

$$\tfrac{1}{2}S_8 + S_4N_4 + 6AsF_5 \xrightarrow{\text{trace } Br_2} 4[S_2N][AsF_6] + 2AsF_3 \quad (4)$$

$$[SN][AsF_6] + \tfrac{1}{8}S_8 \longrightarrow [S_2N][AsF_6] \quad (5)$$

and the consequent use of $AgAsF_6$ which is both expensive and hazardous to make[8] (requiring the use of AsF_5).

Although the overall yield of $[S_2N][SbCl_6]$ produced by the present route is low (35%), the accessibility of starting materials, the facility of reaction, and the ease of purification make this route an attractive alternative to those previously published.

Reaction of $(NSCl)_3$, $FeCl_3$, *and Sulphur* (1:3:3).—This experiment was undertaken to compare the roles of $SbCl_5$ and $FeCl_3$ in similar reactions. The major products isolated were $[S_6N_4][FeCl_4]_2$ and an insoluble residue (largely $FeCl_3$) which exhibited no i.r. absorptions between 4 000 and 400 cm^{-1}. $[S_6N_4][FeCl_4]_2$ has previously been reported as forming green crystals in unspecified yield from the reaction between $FeCl_3$ and S_4N_4 in methylene chloride; the crystal structure has been determined.[15]

The preferential formation of the $S_6N_4^{2+}$ salt can be rationalised on the basis of the weaker Lewis acidity of $FeCl_3$ towards the Cl in a precursor, S=N–SCl (as yet unknown); *i.e.* all S_2N^+ product reacts by cycloaddition across the S=N bond in this supposed intermediate with elimination of SCl, hence giving S_2Cl_2; the SNSCl may be present as an adduct. This possible mechanism is summarised in the Scheme.

$$\left.\begin{array}{r}\tfrac{1}{3}(\mathrm{NSCl})_3 + \mathrm{FeCl_3} + \mathrm{S} \longrightarrow \mathrm{SNS^+FeCl_4^-} \\ \tfrac{1}{3}(\mathrm{NSCl})_3 + \mathrm{S} \longrightarrow \mathrm{S{=}N{-}SCl}\end{array}\right\} \begin{array}{l}\longrightarrow \tfrac{1}{2}[\mathrm{S_6N_4}][\mathrm{FeCl_4}]_2 \\ + \tfrac{1}{2}\mathrm{S_2Cl_2}\end{array}$$

Scheme.

The presence of intermediate SNSCl has previously been suspected in the formation of $S_6N_4Cl_2$ from S_4N_3Cl and SO_2.[16] The experimental molar ratio of reactants $(NSCl)_3:FeCl_3:S$ of 2:6:6 differs from that in the Scheme (2:3:6) in that it provides excess $FeCl_3$ (as found). The product formed comprised a red-brown microcrystalline solid and a green, metallic crystalline solid. Extraction with CH_2Cl_2 yielded green metallic crystals as the sparingly soluble product (identified by i.r. and e.s.r. spectroscopy as an $S_6N_4^{2+}$ compound) together with a small amount of brown, amorphous material. Extraction of a further portion of the crude mixture yielded $[S_6N_4][FeCl_4]_2$ as the soluble product (together with some brown material) and an insoluble brown microcrystalline solid, largely $FeCl_3$. Further purification was not attempted. The nature of the intermediates in these reactions is the subject of further study.

Conclusions

$[S_2N][SbCl_6]$ is prepared by reaction of $(NSCl)_3$, $SbCl_5$, and S_8 in molar ratio $1:3:\frac{3}{8}$ using either $SOCl_2$ or CH_2Cl_2 as solvents. The facility of reaction and ease of purification compensate for the moderate yield. $[S_6N_4][FeCl_4]_2$ was the main product from the corresponding reaction using $FeCl_3$. Other S_2N^+ salts should be preparable by this synthetic method and the preparation of sulphur–nitrogen–selenium cations by reactions with elemental selenium may also be possible.

Experimental

General.—Purification procedures for $FeCl_3$, $SbCl_5$, and $SOCl_2$ have been described previously.[2] $(NSCl)_3$ was prepared according to the literature method[17] and purified by extraction with dry CCl_4. Liquid SO_2 (B.D.H.) was distilled from P_4O_{10} and CaH_2 before use. Sulphur was dried *in vacuo* before use. All glassware was oven dried (*ca.* 100 °C). The closed extractor used in the purification procedures has been described previously.[16] Infrared spectra were recorded as Nujol or hexachlorobutadiene mulls between KBr plates on a Perkin-Elmer type 577 grating spectrophotometer. Raman spectra of crystalline samples, sealed under nitrogen in glass capillaries, were recorded on a Cary 82 spectrophotometer (Spectra Physics 164 laser, 5 145 Å exciting line). Mass spectra were recorded on a V.G. Analytical 7070E mass spectrometer, using electron impact (70 eV, $\approx 1.0 \times 10^{-17}$ J) ionization, at 250 °C with an accelerating potential of 6 kV; samples sealed under nitrogen in glass capillaries were introduced by direct insertion.

Reaction of $(NSCl)_3$, $SbCl_5$ *and Sulphur* (1:3:3).—(*a*) *In thionyl chloride.* $(NSCl)_3$ (1.22 g, 5 mmol) was placed together with a Teflon-coated stirring bar in a twin-necked round-bottomed flask (50 cm^3). $SOCl_2$ (30 cm^3) was syringed in against a counter-flow of dry nitrogen; after all the solid had dissolved, to give a yellow solution, $SbCl_5$ (3.42 g, 1.46 cm^3, 15 mmol) was also syringed in. Immediate reaction occurred (at room temperature, 20 °C) to give a thick, pale orange precipitate which was stirred for a further 30 min. The major constituent of this precipitate was shown by Raman spectroscopy to be $[S_4N_4][SbCl_6]_2$.[18] On addition of sulphur (0.48 g, 15 mmol), the mixture became black, turning slowly to very dark green and after vigorous stirring for 3 h, a pale yellow microcrystalline precipitate had formed. The mixture was stirred for a further 21 h and filtered to yield a pale yellow-green insoluble solid, containing a few large orange crystals (3.95 g) and a dark green solution. No further precipitation from the solution occurred on cooling to −15 °C. Evaporation of the filtrate *in vacuo* yielded a brown-green, slightly sticky solid containing crystals (0.95 g, mostly $[S_3N_2Cl][SbCl_6]$ but containing a little $[S_2N][SbCl_6]$). Extraction of part of the insoluble solid (2.5 g from the total of 3.95 g) with SO_2 gave a soluble brown crystalline solid (mostly $[NS_2Cl_2][SbCl_6]$, 1.4 g) and a pale yellow insoluble solid ($[S_2N][SbCl_6]$, 1.1 g). The products were identified by i.r. and Raman spectroscopy. Some discrepancy between the total weight of reactants (5.12 g) and the total weight of crude products (4.9 g) is to be expected due to loss of unreacted $SbCl_5$ from the system. Yields: 2.5 g of crude product yielded 1.1 g $[S_2N][SbCl_6]$, therefore 3.95 g of crude product contained 1.74 g (28%); using a similar deduction the total amount of $[NS_2Cl_2][SbCl_6]$ produced was 2.2 g; $[S_3N_2Cl][SbCl_6]$, 0.95 g. $[S_2N][SbCl_6]$: i.r., $\nu_{max.}$ at 1 485vs, 372vs, and 340vs cm^{-1} (*cf.* ref. 13); Raman, $\nu_{max.}$ at 770vw, 708vw (sh), 692w, 333s, 298w, 190 (sh), 180m, 80s, 68 (sh), 58vs, and 28s cm^{-1} (*cf.* ref. 13). Brown SO_2-soluble crystals (mostly $[NS_2Cl_2][SbCl_6]$): i.r., $\nu_{max.}$ at 1 130m, 1 000w, 940vw, 748vw, 720vw, 690m, 652m, 570w, 515vs, 492vs, 451vw, and 442w cm^{-1} (*cf.* ref. 3; the value at 520 cm^{-1} is a misprint and should be 500 cm^{-1}). Reaction solubles remaining after removal of solvent (mostly $[S_3N_2Cl][SbCl_6]$ with some $[S_2N][SbCl_6]$): i.r., $\nu_{max.}$ at 1 490m (S_2N^+), 1 005vw, 940m, 749m, 715m, 695vs, 575s, 470w, 445m (sh), and 420m (sh) {*c.f.* $[S_3N_2Cl][FeCl_4]$ (ref. 19): 1 156vs, 1 110w, 1 017w, 997w, 938vs, 891vw, 759w, 742s, 717s, 574s, 463s, 458s, 418vs, 379vs, 331m, 324m, and 304s cm^{-1}}.

(*b*) *In methylene chloride.* A similar procedure to (*a*) above was followed using $(NSCl)_3$ (1.22 g, 5 mmol), $SbCl_5$ (3.42 g, 1.46 cm^3, 15 mmol), and sulphur (0.48 g, 15 mmol) in CH_2Cl_2 (30 cm^3). On addition of the sulphur to the intermediate precipitate, a dark blue-black colour formed almost immediately and the mixture was heated to reflux with continuous stirring. The reaction mixture gradually became dull orange (2 h) and was refluxed for a further 1 h. Cooling (0 °C) and filtration yielded a dull yellow-orange microcrystalline solid (4.25 g) and a red solution. Complete removal of solvent yielded a sticky red solid (*ca.* 0.5 g) from which a few highly refracting, colourless, volatile crystals separated (*ca.* 0.06 g).

Purification of the crude product (4.25 g) was by exhaustive extraction with SO_2, yielding $[S_2N][SbCl_6]$ (2.2 g, 35%, yellow) (Found: Cl, 52.3; N, 3.6; S, 16.1; Sb, 29.4. Cl_6NS_2Sb requires Cl, 51.6; N, 3.4; S, 15.5; Sb, 29.5%) and $[NS_2Cl_2][SbCl_6]$ (2.03 g, orange-brown). $[S_2N][SbCl_6]$: i.r., $\nu_{max.}$ at 1 489vs, 375vs, and 345vs cm^{-1} (*cf.* ref. 13); Raman, $\nu_{max.}$ at 720m, 692w, 655w, 334vs, 290w, 170s, 118w, 80vvs, and 70 vs cm^{-1}. Solubles extracted from crude product: i.r. $\nu_{max.}$ at 1 130m ($NS_2Cl_2^+$), 1 005w, 940m, 855w, 745m, 720m (all $S_3N_2Cl^+$), 695s ($S_3N_2Cl^+$, $NS_2Cl_2^+$), 652m ($NS_2Cl_2^+$), 570s ($S_3N_2Cl^+$, $NS_2Cl_2^+$), 520vs, 495m (both $NS_2Cl_2^+$), 470m, and 420s cm^{-1} (both $S_3N_2Cl^+$). Sticky red CH_2Cl_2–soluble material: i.r., $\nu_{max.}$ at *ca.* 1 430m (NH_4^+), 1 170m,br, 1 040m (sh) ($S_4N_4\cdot SbCl_5$), 1 035m, ($S_4N_4\cdot SbCl_5$), 1 005s ($S_3N_2Cl^+$), 970s (sh) ($S_4N_4\cdot SbCl_5$), 960s (sh) ($S_3N_2Cl^+$), 915w,br, 805w ($S_4N_4\cdot SbCl_5$), 780w ($S_4N_4\cdot SbCl_5$), 750s, 720vs, 695vs, 620w, 570s (all $S_3N_2Cl^+$), 515m ($S_4N_4\cdot SbCl_5$), 470m, and 450s cm^{-1} (both $S_3N_2Cl^+$) (see ref. 12 for spectrum of $S_4N_4\cdot SbCl_5$). Clear volatile crystals, tentatively identified as $NH_3\cdot SbCl_3$: i.r. (ground powder between KBr plates), $\nu_{max.}$ at *ca.* 3 550m,br (νNH_3), 1 605s, ($\delta_{asym}NH_3$), 1 390m ($\delta_{sym}NH_3$), and 700m cm^{-1} (ρNH_3); Raman (clear volatile crystals), $\nu_{max.}$ at 345vs, 320s, 172m, 158m, 148m, 109w, 70m, 58m, and 42m cm^{-1}; mass spectrum, $m/e = 227$ (11.8, $SbCl_3^+$), 192 (100, $SbCl_2^+$), 158 (8.8, $SbCl^+$), 121 (8.47, Sb^+), and 35 (14.99%, Cl^+).

Reaction of $(NSCl)_3$, $FeCl_3$, *and Sulphur* (1:3:3).—A similar procedure to that outlined above was followed using $(NSCl)_3$ (1.22 g, 5 mmol), $FeCl_3$ (2.43 g, 15 mmol), and sulphur (0.48 g, 15 mmol) in CH_2Cl_2 (*ca.* 30 cm^3) at 20 °C. Addition of $FeCl_3$ to the yellow-green solution of $(NSCl)_3$ in CH_2Cl_2 yielded a green-brown precipitate and a dark red solution. Elemental sulphur was added after stirring for 3 h; the mixture darkened further and was stirred for 5 d after which time it consisted of a dark red solution and a dark solid containing green, reflective crystals. Filtration and removal of solvent yielded a mixture of brown and green crystals as the insoluble product (3.42 g) and a dark brown sticky solid as the soluble product (0.15 g). The total weight loss of 0.56 g may be ascribed to removal of S_2Cl_2, formed according to the Scheme.

The crude product (2.85 g) was extracted with CH_2Cl_2 (5 d) to yield a shiny green crystalline solid (2.48 g) together with some sticky brown material. The i.r. spectra of the shiny green solid [$\nu_{max.}$ at 970vs, 940m (sh), 735m (sh), 715vs, 570s, 470vw, and 452s cm^{-1}; *cf.* $S_6N_4Cl_2$ [16]] and the crude product ($\nu_{max.}$ at 965s, 710s, 565s, 448m, and 390s cm^{-1}) were almost identical and a small portion of the former was used for e.s.r. analysis. A portion of crude product (1.18 g) was extracted briefly (2 h) with SO_2 to yield a brown microcrystalline solid (0.35 g) as the insoluble product [Found: Fe, 36.1; Cl, 59.3% (Fe:Cl = 1:2.6)] and a green solid together with some brown material (0.72 g) as the soluble product. The i.r. spectrum of the solubles was identical with those of the crude material and the crystals extracted by CH_2Cl_2; the i.r. spectrum of the brown solid showed no absorptions between 4 000 and 400 cm^{-1}.

Infrared spectrum of solubles: $\nu_{max.}$ at 1 620w (?), 1 030m,br ($S_4N_4\cdot FeCl_3$), 970s ($S_3N_2Cl^+$, $S_4N_4\cdot FeCl_3$), 810s,br ($S_4N_4\cdot FeCl_3$), 730 (sh), 715s, 695s ($S_3N_2Cl^+$), 680 (sh), 570vs ($S_3N_2Cl^+$), 520w ($S_4N_4\cdot FeCl_3$), 485m, and 450m cm^{-1} (both $S_3N_2Cl^+$) (*cf.* $[S_3N_2Cl][FeCl_4]$ [18]); i.r. data unavailable for $S_4N_4\cdot FeCl_3$ but see ref. 12 for related S_4N_4 adducts.

Acknowledgements

We wish to thank the University of Durham for a senior demonstratorship (A. G. K.), Mr. R. Plumb for technical support, Mr. R. Coult for analyses, and Dr. L. H. Sutcliffe for e.s.r. spectra.

References

1 'Gmelin Handbook of Inorganic Chemistry,' 8th edn., 'Sulphur, Sulphur-Nitrogen Compounds,' Springer, Berlin, 1985, vol. 2, and refs. therein.
2 A. J. Banister and H. G. Clarke, *Inorg. Synth.*, 1977, **17**, 188.
3 G. G. Alange, A. J. Banister, and P. J. Dainty, *Inorg. Nucl. Chem. Lett.*, 1979, **15**, 175.
4 O. Glemser, B. Krebs, J. Wegener, and E. Kindler, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 598.
5 R. Mews, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 691.
6 R. G. Hey, Ph.D. Thesis, University of Durham, 1980.
7 R. Mews, personal communication, cited in ref. 10.
8 A. Apblett, A. J. Banister, D. Biron, A. G. Kendrick, J. Passmore, M. J. Schriver, and M. Stojanac, *Inorg. Chem.*, 1986, **25**, 4451.
9 A. J. Banister, R. G. Hey, G. K. MacLean, and J. Passmore, *Inorg. Chem.*, 1982, **21**, 1679.
10 G. K. MacLean, J. Passmore, M. N. S. Rao, M. J. Schriver, P. S. White, D. Bethell, R. S. Pilkington, and L. H. Sutcliffe, *J. Chem. Soc., Dalton Trans.*, 1985, 1405 and refs. therein.
11 W. V. F. Brooks, G. K. MacLean, J. Passmore, P. S. White, and C. M. Wong, *J. Chem. Soc., Dalton Trans.*, 1983, 1961.
12 K. J. Wynne and W. L. Jolly, *Inorg. Chem.*, 1967, **6**, 107; P. J. Ashley and E. G. Torrible, *Can. J. Chem.*, 1969, **47**, 2587; R. C. Paul, C. L. Arora, and K. C. Malhotra, *Aust. J. Chem.*, 1971, **24**, 1673; G. G. Alange and A. J. Banister, *J. Inorg. Nucl. Chem.*, 1978, **40**, 203.
13 R. Faggiani, R. J. Gillespie, C. J. L. Lock, and J. D. Tyrer, *Inorg. Chem.*, 1978, **17**, 2975.
14 U. Thewalt, K. Berhalter, and P. Müller, *Acta Crystallogr., Sect. B*, 1982, **38**, 1280.
15 U. Thewalt and M. Burger, *Z. Naturforsch., Teil B*, 1981, **36**, 293.
16 R. W. H. Small, A. J. Banister, and Z. V. Hauptman, *J. Chem. Soc., Dalton Trans.*, 1984, 1377.
17 W. J. Jolly and K. D. Maguire, *Inorg. Synth.*, 1967, **9**, 102.
18 R. J. Gillespie, J. F. Sawyer, D. R. Slim, and J. D. Tyrer, *Inorg. Chem.*, 1982, **21**, 1296.
19 A. J. Banister and P. J. Dainty, *J. Chem. Soc., Dalton Trans.*, 1972,

Received 14*th July* 1986; *Paper* 6/1462