Preparation and *X*-Ray Crystal Structures of Copper(I) Complexes of the S_3N^- Ion

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Summary The first complexes of copper(I) and silver(I) with the S_3N^- ligand have been prepared by the reaction of $PPN^+ S_3N^-$ with copper(I) chloride or silver nitrate in acetonitrile; the *X*-ray crystal structures of $PPN^+ Cu(S_3N)_2^-$, $(Ph_3P)_2Cu(S_3N)$, and $PPN^+ ClCu(S_3N)^-$ show that the bidentate S_3N^- ligand is bonded to the metal through two sulphur atoms in these complexes.

IT has been known since 1958 that the reaction of transition metal halides, *e.g.* Ni,[1] Co,[2] and Pd,[2] with S_4N_4 in methanol produces complexes of the type $M(S_3N)_2$. However, despite recent improvements in the preparative and purification procedures,[3] these interesting compounds are available only in milligram quantities. In fact, the major products of S_4N_4/MX_2 reactions (M = Ni, Co, Pd, Pt) are complexes of the $S_2N_2H^-$ ligand.[1–3] In contrast, the reaction of copper halides with S_4N_4 produces compounds in which S_4N_4[4] or S_2N_2[5] are co-ordinated as bridging ligands through nitrogen atoms to copper. In principle, the availability of salts of the S_3N^- anion[6] should provide a more direct route to metal complexes of this ligand *via* metathetical reactions. We report here the application of this synthetic route to the preparation of the first copper(I) and silver(I) complexes of S_3N^- and the structural characterization of the co-ordinated S_3N^- ligand in two of the copper(I) complexes.

Copper(I) chloride (2·5 mmol) was added to an orange solution of $PPN^+ S_3N^-$, prepared from $PPN^+ S_4N^-$ (2·1 mmol) and triphenylphosphine (2·9 mmol) in dry acetonitrile (30 ml).[†] After $2\frac{1}{2}$ h, solvent was removed *in vacuo* and the deep red residue was washed with diethyl ether (5 × 100 ml). Several fractional recrystallizations of the residue from MeCN/Et_2O gave pure $PPN^+ ClCu(S_3N)^-$ (23% yield).[‡] The u.v.–visible spectrum (MeCN) has absorption maxima at 337 ($\epsilon = 2{\cdot}7 \times 10^3$ $dm^3 mol^{-1} cm^{-1}$) and 494 nm ($3{\cdot}5 \times 10^3$).

Addition of copper(I) chloride (1·2 mmol) to *an excess* of $PPN^+ S_3N^-$ (*ca.* 2·1 mmol) in acetonitrile (30 ml) produced a dark blue–green, microcrystalline precipitate. After $2\frac{1}{2}$ h, this product was filtered off, washed with toluene and diethyl ether, and identified as $PPN^+ Cu(S_3N)_2^-$ (46% yield).[‡] The u.v.–visible spectrum of $PPN^+ Cu(S_3N)_2^-$ in MeCN has absorption maxima at 356 ($\epsilon = 5{\cdot}8 \times 10^3$ $dm^3 mol^{-1} cm^{-1}$) and 603 nm ($3{\cdot}2 \times 10^3$).

The corresponding complex of silver(I), $PPN^+ Ag(S_3N)_2^-$, was obtained as orange crystals (17%) by the reaction of $PPN^+ S_3N^-$ with silver nitrate (1 : 1 molar ratio) in acetonitrile.[‡][§]

Addition of triphenylphosphine (0·84 mmol) to a solution of $PPN^+ ClCu(S_3N)^-$ (0·42 mmol) in acetonitrile (15 ml) produced a royal-blue solid identified as $(Ph_3P)_2Cu(S_3N)$ (81%).[‡] The u.v.–visible spectrum of the yellow solution of $(Ph_3P)_2Cu(S_3N)$ in MeCN has absorption maxima at 319 ($\epsilon = 3{\cdot}5 \times 10^3$ $dm^3 mol^{-1} cm^{-1}$) and 446 nm ($5{\cdot}6 \times 10^3$).

The molecular structures of these new complexes of copper(I) have been determined by *X*-ray crystallography.

Crystal data: $C_{36}H_{30}NP_2S_3Cu$, $M = 698{\cdot}3$, monoclinic, space group $P2/c$, $a = 11{\cdot}752(6)$, $b = 8{\cdot}638(2)$, $c = 16{\cdot}310(9)$ Å, $\beta = 104{\cdot}54(2)°$, $U = 1602(1)$ Å^3, $Z = 2$, $D_c = 1{\cdot}45$ g cm^{-3}, μ(Mo-K_α) = 10·50 cm^{-1}. Crystal dimensions 0·13 × 0·22 × 0·21 mm. A total of 3473 unique reflections of which 1158 had $I \geqslant 3\sigma(I)$ were measured at −100(5) °C. The data were collected on a CAD4F diffractometer equipped with a graphite monochromator using Mo-K_α radiation ($\lambda = 0{\cdot}71069$ Å) and operated in the ω–2θ scan mode. The structure was solved by direct methods; the molecule is positioned on a two-fold axis which imposes disorder on the S_3N^- ligand. The packing disorder was modelled with two sulphur atoms and two nitrogen atoms with occupancies of 50% and the structure was refined by full-matrix least squares techniques to give a final unweighted R value of 0·045.[¶]

Crystal data: $(C_{36}H_{30}NP_2)^+(N_2S_6Cu)^-$, $M = 822{\cdot}5$, monoclinic, space group $C2/c$, $a = 15{\cdot}241(6)$, $b = 16{\cdot}869(5)$, $c = 14{\cdot}942(7)$ Å, $\beta = 110{\cdot}10(2)°$, $U = 3608(2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}456$ g cm^{-3}, $D_c = 1{\cdot}47$ g cm^{-3}, μ(Mo-K_α) = 10·53 cm^{-1}. Crystal dimensions 0·27 × 0·25 × 0·20 mm. A total of 3168 unique reflections of which 1284 had $I \geqslant 3\sigma(I)$ were measured at −100(5) °C. The structure was solved by direct methods; the copper atom and the nitrogen atom of the PPN^+ cation are positioned on a two-fold axis. The symmetry imposes a packing disorder on the S_3N^- ligands which was modelled as above and the structure was refined by full-matrix least squares techniques to give a final unweighted R value of 0·031.[¶]

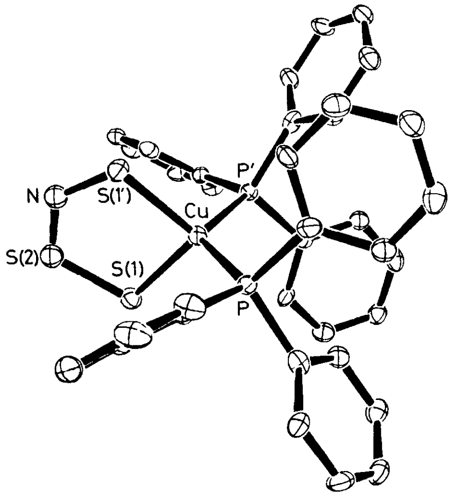

FIGURE 1. ORTEP drawing (50% probability ellipsoids) of $(Ph_3P)_2Cu(S_3N)$ showing the atomic numbering scheme. The bond distances and bond angles (e.s.d.s in parentheses) in the $Cu(S_3N)$ unit are: Cu–S(1), 2·304(2); S(1)–S(2), 2·058(4); S(2)–N, 1·593(12); N–S(1'), 1·541(13) Å; ∠S(1)–Cu–S(1'), 94·90(8); Cu–S(1)–S(2), 97·4(1); S(1)–S(2)–N, 114·9(5); S(2)–N–S(1'), 124·9(8); N–S(1')–Cu, 107·9(5)°.

Accurate structural parameters for the $ClCu(S_3N)^-$ anion could not be obtained owing to large thermal motion in the anion. However, an *X*-ray structural analysis to $R = 0{\cdot}130$ has clearly established that this anion contains a bidentate S_3N^- ligand with trigonal geometry at copper.

The structures of $(Ph_3P)_2Cu(S_3N)$ and the $Cu(S_3N)_2^-$ ion are shown in Figures 1 and 2, respectively. In both complexes the S_3N^- ligands bind to copper in a bidentate fashion *via* two sulphur atoms[7] and the geometry about copper is approximately tetrahedral. The structural parameters of the co-ordinated S_3N^- ligand in these complexes show

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[†] The optimum molar ratio for the preparation of $PPN^+ S_3N^-$ from the reaction of $PPN^+ S_4N^-$ with triphenylphosphine is *ca.* 1 : 1·4, see also ref. 6; PPN = $(Ph_3P)_2N$.

[‡] Satisfactory analytical data were obtained for all new compounds reported in this communication.

[§] The stoicheiometry of this reaction was varied to optimise the yield of $PPN^+ Ag(S_3N)_2^-$. For a 2 : 1 ratio (S_3N^- : $AgNO_3$) the yield dropped to 12% and oxidation of S_3N^- to S_4N^- was observed. When an excess of $AgNO_3$ was used, the major products were S_4N_4 and silver(I) sulphide.

[¶] The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

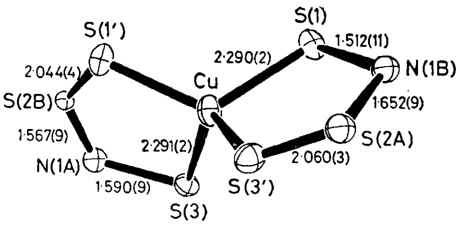

FIGURE 2. ORTEP drawing (50% probability ellipsoids) of the anion in PPN$^+$ Cu$(S_3N)_2^-$ showing the atomic numbering scheme and bond distances. Bond angles (e.s.d.s in parentheses) are: S(1)–Cu–S(3), 94·28(6); S(1′)–Cu–S(1), 118·46(7); S(3)–Cu–S(3′), 121·35(7); Cu–S(1)–N(1B), 111·1(3); Cu–S(3)–N(1A), 108·8(3); Cu–S(1′)–S(2B), 98·0(1); Cu–S(3′)–S(2A), 98·1(1); S(1)–N(1B)–S(2A), 121·8(5); S(3)–N(1A)–S(2B), 122·1(6); N(1B)–S(2A)–S(3′), 114·6(4); N(1A)–S(2B)–S(1′), 116·2(4)°.

similar trends which are distinctly different from those found in the only previous structural determination of a metal complex of this ligand, *viz.* Pd$(S_3N)_2$.[8]** Thus the S–S bond distances are 2·04—2·06 Å [*cf.* 1·93 and 1·96 Å in Pd$(S_3N)_2$] and the angles ∠M–S–S are 97·4—98·8° (*cf.* 103·1 and 104·9°).[8] The S–N bond distances are unequal at 1·51—1·59 and 1·57—1·65 Å, the shorter one involving the sulphur bonded directly to copper. In contrast, in Pd$(S_3N)_2$ the longest S–N bonds (1·65 and 1·69 Å) involve this sulphur atom and the other S–N distances were significantly shorter (1·48 and 1·58 Å). The Cu–S distances of 2·29—2·30 Å are typical for copper(I) bonded to sulphur ligands.[9] The 5-membered Cu(S_3N) ring in $(Ph_3P)_2$Cu(S_3N) is essentially planar, whereas in Cu$(S_3N)_2^-$ one S atom in each ring [S(3) and S(2B)] lies out of the plane through the other four atoms by 0·10 and 0·12 Å, respectively.

The availability of complexes of the S_3N^- ion with copper(I) and silver(I) by the simple preparative procedures described above should enable a study of the chemistry of the coordinated S_3N^- ligand to be undertaken.

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** Since the submission of this communication a paper describing the preparation and molecular structure of Co$(NO)_2(S_3N)$ has appeared (M. Herberhold, L. Haumaier, and U. Schubert, *Inorg. Chim. Acta*, 1981, **49**, 21). In this complex d(S–S) = 2·00 Å, ∠Co–S–S = 103·5°, and the S–N bond lengths are 1·63 and 1·55 Å, the longer one involving the sulphur bonded directly to copper.

[1] T. S. Piper, *J. Am. Chem. Soc.*, 1958, **80**, 30.

[2] J. Weiss and U. Thewalt, *Z. Anorg. Allg. Chem.*, 1966, **346**, 234.

[3] J. D. Woollins, R. Grinter, M. K. Johnson, and A. J. Thomson, *J. Chem. Soc., Dalton Trans.*, 1980, 1910.

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[6] J. Bojes and T. Chivers, *J. Chem. Soc., Chem. Commun.*, 1980, 1023.

[7] In recent reviews the S_3N^- ligand was represented as co-ordinated through the nitrogen and one sulphur atom to the metal in Ni$(S_3N)_2$: H. J. Emeléus, *Endeavour*, 1973, **32**, 76; H. W. Roesky, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 239.

[8] J. Weiss and H. S. Neubert, *Z. Naturforsch., Teil B*, 1966, **21**, 286; the structure of Pd$(S_3N)_2$ reported in this communication is not very accurate (R = 12·7%).

[9] See for example, I. F. Taylor, Jr., M. S. Weininger, and E. L. Amma, *Inorg. Chem.*, 1974, **13**, 2835; G. W. Hunt, E. A. H. Griffith, and E. L. Amma, *ibid.*, 1976, **15**, 2993.