Preparation, Crystal Structure, and Spectroscopic Studies of $[NPr^{n}_{4}]_2[(PhS)CuS_2MoS_2]$ and $[NPr^{n}_{4}]_2[(PhS)CuS_2MoS_2Cu(SPh)]$,† containing Benzenethiolatocopper(I)–Tetrathiomolybdate(VI) Complex Anions

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The complexes $[(PhS)CuS_2MoS_2]^{2-}$ and $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ have been prepared by the reaction of KSPh on the corresponding cyano-complex and isolated as their $[NPr^{n}_{4}]^{+}$ salts. The complex $[NPr^{n}_{4}]_2[(PhS)CuS_2MoS_2]$ crystallises in the space group $P2_1/c$ with a = 16.534(2), b = 16.608(2), c = 14.863(2) Å, β = 104.60(1)°, and Z = 4, while $[NPr^{n}_{4}]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ crystallises in the space group $C2/c$ with a = 17.064(2), b = 15.646(2), c = 18.448(2) Å, β = 110.47(1)° and Z = 4. The structures were solved by Patterson and Fourier techniques from 4 495 and 2 404 diffractometer data, respectively, and refined to respective R values of 0.060 and 0.051. The anion $[(PhS)CuS_2MoS_2]^{2-}$ involves an essentially tetrahedral $[MoS_4]^{2-}$ moiety co-ordinated as a bidentate ligand to a copper(I) atom [Mo-S(terminal) = 2.162(6), Mo-S(Cu) = 2.221(9), Cu-S = 2.211(13), and Mo ··· Cu = 2.636(1) Å], the third position of the trigonal planar co-ordination about the copper being occupied by a benzenethiolate group [Cu-S = 2.188(2) Å]. The anion $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ has crystallographic C_2 symmetry and involves the co-ordination of an essentially tetrahedral $[MoS_4]^{2-}$ moiety to two copper(I) atoms [Mo-S = 2.206(6), Cu-S = 2.212(2), and Mo ··· Cu = 2.632(1) Å], with each trigonal planar copper(I) atom also participating in a Cu–SPh bond of length 2.171(2) Å. These structural data have been used to interpret ^{95}Mo and ^{1}H n.m.r., vibrational, and u.v.-visible spectroscopic data.

The tetrathiometallate anions of molybdenum(VI) and tungsten(VI) are useful and versatile reagents, the development of their chemistry owing much to Muller *et al.*[1] One of their important functions is the co-ordination, often as a bidentate ligand, to the later transition metals, Fe,[2] Co,[3] Ni,[4] Pd,[5] Pt,[5] Cu,[6-10] Ag,[11] Au,[12], Zn,[13] Cd,[1] and Hg,[1] and to Sn.[14] Other syntheses employing these $[MS_4]^{2-}$ ions can lead to the formation of complexes containing M'_3MS_4 cubane-like clusters, which have been characterised by *X*-ray crystallography for M′ = Fe; [15] related cubane-like (M'_3MS_3Cl) and $M'_4M_2S_6$ cages have also been identified [1,9,16-18] for M′ = Cu and Ag. The electronic structures of these complexes are of interest, in that they involve a significant amount of electron delocalisation over the M′–S–M network. Furthermore, some of these complexes (for M = Mo) have biological relevance. In the case of iron, the complexes, particularly those with Fe_3MoS_4 cubane-like cores,[15] serve as possible models for the molybdenum centre of the iron–molybdenum cofactor of the nitrogenase molybdoferredoxin protein. For copper, the complexes [6-10,16] improve the chemical basis for interpreting the copper–thiomolybdate interactions responsible, at least in part, for the biological antagonism between copper and molybdenum, which leads to copper deficiency, particularly in ruminant animals.[19,20]

Herein, we report the preparation, spectroscopic, and structural characterisation of $[(PhS)CuS_2MoS_2]^{2-}$ and $[(PhS)CuS_2MoS_2(SPh)]^{2-}$, new additions to the family of discrete copper(I)–tetrathiomolybdate complexes; other members include $[(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)]$,[9] $[(NC)CuS_2MoS_2]^{2-}$, and $[(NC)CuS_2MoS_2Cu(CN)]^{2-}$.[6-8]

Experimental

Reactions were carried out under an atmosphere of purified dinitrogen, using Schlenk tubes, with solvent and solution transfers being accomplished through Gallenkamp Suba-seal stoppers by syringe or siphon-tube. Acetonitrile (Hopkin and Williams reagent grade) was distilled from CaH_2 under a dinitrogen atmosphere; sodium-dried diethyl ether was used. Thiophenol (Koch-Light) was distilled before use and converted into its potassium salt by reaction with potassium metal in tetrahydrofuran.

Microanalyses were carried out by Mr. M. Hart and his staff in the University of Manchester Microanalytical Chemistry Department. Infrared spectra were recorded, for Nujol mulls of the samples between CsI plates, in the range 4 000—200 cm^{-1} on a Perkin-Elmer 577 grating spectrometer. Raman spectra were obtained using 5145 Å excitation from an argon ion laser and recorded on a Cary 82 instrument by Dr. R. S. Alexander. Ultraviolet-visible spectra were recorded on a Perkin-Elmer 402 spectrometer. Proton n.m.r. spectra were measured for *ca.* 0.1 mol dm^{-3} solutions in $(CD_3)_2SO$ at 300 MHz on a Varian SC-300 instrument, with the help of Mr. D. Moorcroft. 26.08 MHz ^{95}Mo n.m.r. spectra were obtained by Dr. B. E. Mann using the S.E.R.C., Sheffield University Bruker WH-400 N.M.R. Service.

Preparation of $[NPr^{n}_{4}]_2[(PhS)CuS_2MoS_2]$.—The complex $[NPr^{n}_{4}]_2[(NC)CuS_2MoS_2]$ [6,8] (1.00 g, 1.46 mmol) was dissolved in MeCN (7.5 cm^3) and solid KSPh (0.24 g, 1.62 mmol) added. The mixture was stirred overnight at room temperature and then the orange-red solution was separated from the white precipitate by filtration. Addition of Et_2O to the orange-red solution precipitated *ca.* 0.5 g (45%) of the product, con-

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† Bis(tetra-n-propylammonium) benzenethiolato(tetrathiomolybdenio-*SS′*)cuprate(2−) and bis(tetra-n-propylammonium) bis(benzenethiolato)(μ-tetrathiomolybdenio-*SS* : *S″S‴*)-dicuprate-(2−).

Supplementary data available (No. SUP 23502, 48 pp.): structure factors, thermal parameters, H-atom co-ordinates. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Crystal structure determinations

	$[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ (1) $C_{30}H_{61}CuMoN_2S_5$	$[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ (2) $C_{36}H_{66}Cu_2MoN_2S_6$
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
a/Å	16.534(2)	17.064(2)
b/Å	16.608(2)	15.646(2)
c/Å	14.863(2)	18.448(2)
β/°	104.60(1)	110.47(1)
U/Å^3	3 949.5	4 614.3
Z	4	4
D_c/g cm^{-3}	1.294	1.356
F(000)	1 623.6	1 967.5
μ/cm^{-1}	11.24	14.64
Crystal size/mm	0.35 × 0.19 × 0.46	0.12 × 0.27 × 0.46
$2\theta_{max.}$/°	50	50
Transmission factors	0.625—0.670	0.721—0.865
Reflections measured	7 214	4 221
Unique data $[F > 4\sigma(F)]$	4 495	2 404
Refined parameters	376	225
R [a]	0.060	0.051
R' [b]	0.061	0.031
Weighting parameter	0.000 39	0

[a] $R = \Sigma|\Delta|/\Sigma|F_o|$; $\Delta = |F_o| - |F_c|$. [b] $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$.

taminated with a small amount of KSPh. This contamination could be avoided and red, diamond shaped crystals obtained in a slightly lower yield, by careful addition of the Et_2O to incipient crystallisation and subsequent standing at room temperature for several hours (Found: C, 46.8; H, 8.2; Cu, 8.2; Mo, 12.3; N, 3.8; S, 20.4. $C_{30}H_{61}CuMoN_2S_5$ requires C, 46.8; H, 8.0; Cu, 8.3; Mo, 12.5; N, 3.6; S, 20.8%).

The complex $[NPr^n_4]_2[(4\text{-}MeC_6H_4S)CuS_2MoS_2]$ was obtained as a crystalline solid in an analogous manner, from $[NPr^n_4]_2[(NC)CuS_2MoS_2]$ and $K(SC_6H_4Me\text{-}4)$ (Found: C, 47.7; H, 8.2; Cu, 8.4; Mo, 11.8; N, 3.5; S, 20.4. $C_{31}H_{53}CuMoN_2S_5$ requires C, 47.5; H, 8.1; Cu, 8.1; Mo, 12.2; N, 3.5; S, 20.5%).

Preparation of $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$.—The complex $[NPr^n_4]_2[(NC)CuS_2MoS_2Cu(CN)]$[8] (1.00 g, 1.3 mmol) was dissolved in MeCN (5 cm^3) and solid KSPh (0.4 g, 2.7 mmol) added and the mixture stirred overnight at room temperature. The orange-red precipitate thus obtained was separated by filtration and the coloured material extracted into MeCN. This extract was concentrated and the product precipitated in *ca.* 50% yield (0.6 g) by the addition of Et_2O; the material was separated by filtration and dried *in vacuo*. Careful control of the Et_2O addition and the solution temperature, prior to standing for several hours at room temperature, yielded a crystalline product containing dark red rectangular-faced crystals (Found: C, 45.7; H, 7.1; Cu, 13.2; Mo, 10.1; N, 3.2; S, 20.5. $C_{36}H_{66}Cu_2MoN_2S_6$ requires C, 45.9; H, 7.1; Cu, 13.5; Mo, 10.2; N, 3.0; S, 20.4%).

The related compound $[NEt_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]\cdot H_2O$ was prepared *via* an alternative route: KSPh (0.6 g, 3.8 mmol) was suspended in MeCN (*ca.* 25 cm^3) and $[NEt_4]Cl\cdot H_2O$ (0.7 g, 3.8 mmol) added. The white precipitate (KCl) which formed was removed by filtration, the solution evaporated to dryness and $[NEt_4][SPh]$ obtained in essentially quantitative yield. The compound $[(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)]$[9] (0.23 g, 0.2 mmol) was dissolved in MeCN (*ca.* 7 cm^3) and $[NEt_4][SPh]$ (0.2 g, 0.84 mmol) added. The resultant clear red solution was stirred for *ca.* 4 h and a small quantity of a pale red precipitate removed by filtration. The filtrate was concentrated, by evaporation under a reduced pressure at room temperature, and the subsequent careful addition of Et_2O produced a bright red microcrystalline solid in *ca.* 60% yield (0.1 g) (Found: C, 40.0; H, 6.0; Cu, 14.8; Mo, 11.0; N, 3.0; S, 22.2. $C_{28}H_{52}Cu_2MoN_2OS_6$ requires C, 39.6; H, 6.2; Cu, 15.0; Mo, 11.3; N, 3.3; S, 22.7%).

Crystals of $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ (1) and $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ (2), prepared as described above, proved suitable for *X*-ray diffraction studies.

Crystal Structure Determination.—Crystal data are summarized in Table 1. For both complexes, crystals were sealed in glass capillaries and examined at room temperature on a Stoe-Siemens AED diffractometer, with graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å). Unit-cell parameters were refined from 2θ values ($20 < 2\theta < 25°$) of 40 [complex (1)] and 56 [complex (2)] reflections.

Intensity data were measured by a real-time profile-fitting method.[21] Absorption corrections were of an empirical type, based on the measurement of sets of equivalent reflections at various azimuthal angles.

The structures were solved by Patterson and Fourier techniques, and refined with anisotropic thermal parameters to a minimum value of $\Sigma w\Delta^2$, with $w^{-1} = \sigma^2(F) + gF_o^2$; the value of g was optimised in each case during the refinement. Hydrogen atoms were included in the refinement, subject to the constraints: C–H = 0.96 Å, H–C–H = 109.5° in n-propyl groups, aromatic C–H on the external bisectors of C–C–C angles, U(H) = 1.2U(C), where U(C) is the equivalent isotropic thermal parameter of a carbon atom, defined as one-third of the trace of the orthogonalised U_{ij} tensor.[22]

Atomic co-ordinates, bond lengths and angles are given in Tables 2—5.

Results and Discussion

The structure of the anions of $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ (1) and $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ (2), in which the molybdenum lies on a crystallographic C_2 axis, are shown in Figures 1 and 2, respectively. In each anion, the copper and molybdenum atoms have essentially a trigonal planar and a tetrahedral co-ordination geometry, respectively. For both compounds the copper atom lies (to within 0.041 Å) in the plane of the three sulphur atoms and the MoS_2CuS moiety is planar (maximum deviation 0.037 Å).

The Cu–S distances [average 2.20(2) Å] are slightly shorter

Table 2. Atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ (1)

Atom	*x*	*y*	*z*
Mo	2 044(1)	6 086(1)	2 538(1)
Cu	2 433(1)	4 749(1)	3 506(1)
S(1)	2 960(1)	5 153(1)	2 365(1)
S(2)	1 532(1)	5 686(1)	3 704(1)
S(3)	2 646(1)	3 657(1)	4 357(1)
S(4)	2 642(1)	7 247(1)	2 864(1)
S(5)	1 029(1)	6 147(1)	1 301(1)
C(1)	3 023(3)	2 869(4)	3 783(5)
C(2)	3 120(3)	2 921(4)	2 892(5)
C(3)	3 375(4)	2 256(5)	2 462(6)
C(4)	3 555(5)	1 540(5)	2 930(6)
C(5)	3 476(4)	1 483(4)	3 811(6)
C(6)	3 218(4)	2 129(4)	4 253(5)
N(1)	122(2)	3 280(3)	2 034(3)
C(11)	779(3)	3 653(3)	1 608(4)
C(12)	823(4)	3 322(4)	679(4)
C(13)	1 494(5)	3 748(5)	348(5)
C(21)	197(3)	2 377(3)	2 073(4)
C(22)	1 031(4)	2 048(4)	2 615(5)
C(23)	1 025(5)	1 151(4)	2 536(7)
C(31)	278(4)	3 655(3)	2 998(4)
C(32)	−297(4)	3 388(4)	3 590(4)
C(33)	−45(6)	3 815(5)	4 516(5)
C(41)	−764(3)	3 448(3)	1 461(4)
C(42)	−1 024(4)	4 315(4)	1 379(5)
C(43)	−1 935(4)	4 371(5)	855(6)
N(2)	4 079(3)	8 457(3)	1 051(3)
C(51)	4 713(5)	8 795(5)	1 867(5)
C(52)	4 679(6)	8 675(7)	2 761(6)
C(53)	5 287(6)	9 057(6)	3 550(6)
C(61)	4 147(6)	7 540(4)	1 090(6)
C(62)	3 750(7)	7 022(5)	442(6)
C(63)	3 956(6)	6 165(4)	534(7)
C(71)	4 261(6)	8 738(4)	160(6)
C(72)	4 950(6)	8 541(6)	−116(8)
C(73)	5 030(5)	8 793(5)	−1 041(5)
C(81)	3 210(5)	8 728(5)	1 087(6)
C(82)	3 031(5)	9 527(5)	1 207(6)
C(83)	2 199(5)	9 772(6)	1 296(6)

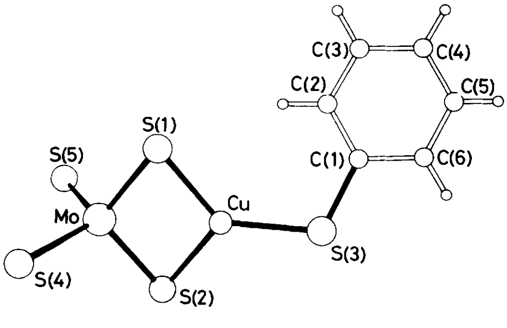

Figure 1. Structure of the anion in $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$

than observed for other compounds in which copper(I) is co-ordinated by three sulphur atoms in a trigonal array. These include $[NEt_4]_2[Cu(SPh)_3]$ [2.25(1) Å],[23] $[PPh_4]_2[Cu(SPh)_3]$ [2.30(4) Å],[24] $[NEt_4][Cu_5(\mu\text{-}SBu^t)_6]$ [2.27(2) Å],[25] $[NMe_4]_2[Cu_5(SPh)_7]$ [2.27(2) Å],[26] $[Cu(SPMe_3)_3][ClO_4]$ [2.259(5) Å],[27] and $[Cu(NN'\text{-ethylenethiourea})_3]_2[SO_4]$ [2.281(1) Å].[28] Furthermore, the Cu–SPh bond lengths [2.188(2) and 2.171(2) Å] obtained in this study are significantly shorter than those given above for $[NMe_4]_2[Cu_5(SPh)_7]$,[26] in which each benzenethiolate group is a μ-ligand, and in $[Cu(SPh)_3]^{2-}$ in which each ligand is terminal.[23,24] A similar, although not quite as marked, reduction in a terminal metal–SPh bond upon co-ordination to $[MoS_4]^{2-}$ has been observed for iron(II), with the average Fe–SPh bond lengths in $[PPh_4]_2[Fe(SPh)_4]$ and $[NEt_4]_2[(PhS)_2FeS_2MoS_2]$ being 2.356(14) Å[29] and 2.309(9) Å,[30,31] respectively. Iron-57 Mossbauer isomer shift values for these two iron complexes [0.66(1)[32] and 0.44(1)[30] mm s^{-1} at 4.2 K, respectively] correspond to a formal +2 oxidation state in the former but some partial charge redistribution, from Fe^{II} to Mo^{VI}, in the latter. Therefore, we tentatively suggest that these $[(PhS)CuS_2MoS_2]^{2-}$ and $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ ions also involve a delocalisation of charge, from Cu^I to Mo^{VI}.

Table 3. Atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses, for $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ (2)

Atom	*x*	*y*	*z*
Mo	0	601(1)	2 500
Cu	1 573(1)	605(1)	3 429(1)
S(1)	561(1)	−214(1)	3 531(1)
S(2)	1 007(1)	1 410(1)	2 390(1)
S(3)	2 874(1)	766(1)	4 157(1)
C(1)	3 281(3)	−195(3)	4 630(3)
C(2)	2 887(3)	−979(4)	4 441(3)
C(3)	3 246(4)	−1 715(4)	4 812(4)
C(4)	4 013(5)	−1 689(5)	5 381(5)
C(5)	4 419(5)	−934(6)	5 585(5)
C(6)	4 057(4)	−190(4)	5 218(4)
N	3 073(2)	3 698(2)	3 598(2)
C(11)	3 502(3)	3 308(3)	3 090(3)
C(12)	3 226(4)	2 416(4)	2 793(4)
C(13)	3 720(5)	2 112(5)	2 313(4)
C(21)	3 229(3)	3 191(3)	4 339(3)
C(22)	4 137(3)	3 119(4)	4 861(3)
C(23)	4 208(4)	2 554(4)	5 557(3)
C(31)	3 419(3)	4 596(3)	3 785(3)
C(32)	3 067(3)	5 129(3)	4 275(3)
C(33)	3 535(5)	5 976(3)	4 453(4)
C(41)	2 130(3)	3 701(3)	3 207(3)
C(42)	1 820(4)	4 180(4)	2 431(3)
C(43)	891(4)	4 155(6)	2 092(5)

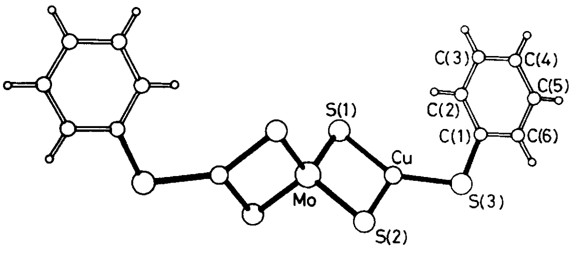

Figure 2. Structure of the anion in $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$

The Cu–S–C angles [111.2(2) and 110.5(2)°] are similar to those obtained for the terminal benzenethiolate groups in $[NEt_4]_2[Cu(SPh)_3]$[23] and $[PPh_4]_2[Cu(SPh)_3]$[24] [average values 114(1)° and 111(3)°, respectively]. This angle, together with the approximate planarity of the MoS_2CuSC moieties (maximum deviation 0.31 Å) in each structure, is not inconsistent with essentially sp^2 hybridisation at the thiolato-sulphur atom. Such a hybridization would permit some $S(p_\pi)$ to $Cu(p,d_\pi)$ donation—*i.e.* into the formally vacant 4*p* orbital on copper, to augment σ bonding over these short Cu–S distances. The bending at the thiolate sulphur introduces an asymmetry in the anions which is also apparent in the dimensions of the MoS_2CuS group. In particular, the (Mo)S–Cu–S(Ph) angle

Table 4. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ (1), with estimated standard deviations in parentheses

Mo···Cu	2.636(1)			S(1)-Mo-S(2)	106.7(1)	S(1)-Mo-S(4)	111.1(1)
Mo-S(1)	2.227(2)	Mo-S(2)	2.214(2)	S(2)-Mo-S(4)	109.6(1)	S(1)-Mo-S(5)	109.8(1)
Mo-S(4)	2.166(2)	Mo-S(5)	2.157(2)	S(2)-Mo-S(5)	108.3(1)	S(4)-Mo-S(5)	111.2(1)
Cu-S(1)	2.198(2)	Cu-S(2)	2.224(2)	S(1)-Cu-S(2)	107.3(1)	S(1)-Cu-S(3)	131.5(1)
Cu-S(3)	2.188(2)	S(3)-C(1)	1.761(7)	S(2)-Cu-S(3)	121.2(1)	Mo-S(1)-Cu	73.1(1)
C(1)-C(2)	1.377(10)	C(1)-C(6)	1.410(9)	Mo-S(2)-Cu	72.9(1)	Cu-S(3)-C(1)	111.2(2)
C(2)-C(3)	1.392(11)	C(3)-C(4)	1.372(12)	S(3)-C(1)-C(2)	124.1(5)	S(3)-C(1)-C(6)	118.3(5)
C(4)-C(5)	1.351(13)	C(5)-C(6)	1.380(11)	C(2)-C(1)-C(6)	117.6(6)	C(1)-C(2)-C(3)	121.0(6)
N(1)-C(11)	1.521(8)	N(1)-C(21)	1.504(7)	C(2)-C(3)-C(4)	120.4(8)	C(3)-C(4)-C(5)	119.4(8)
N(1)-C(31)	1.523(7)	N(1)-C(41)	1.523(6)	C(4)-C(5)-C(6)	121.5(7)	C(1)-C(6)-C(5)	120.1(7)
C(11)-C(12)	1.505(9)	C(12)-C(13)	1.499(12)	C(11)-N(1)-C(21)	111.2(4)	C(11)-N(1)-C(31)	104.8(4)
C(21)-C(22)	1.513(8)	C(22)-C(23)	1.494(9)	C(21)-N(1)-C(31)	112.2(4)	C(11)-N(1)-C(41)	112.3(4)
C(31)-C(32)	1.515(10)	C(32)-C(33)	1.509(10)	C(21)-N(1)-C(41)	105.2(4)	C(31)-N(1)-C(41)	111.2(4)
C(41)-C(42)	1.499(9)	C(42)-C(43)	1.515(9)	N(1)-C(11)-C(12)	116.0(5)	C(11)-C(12)-C(13)	109.8(6)
N(2)-C(51)	1.499(8)	N(2)-C(61)	1.526(9)	N(1)-C(21)-C(22)	115.9(4)	C(21)-C(22)-C(23)	109.4(5)
N(2)-C(71)	1.505(11)	N(2)-C(81)	1.519(10)	N(1)-C(31)-C(32)	116.4(5)	C(31)-C(32)-C(33)	108.8(6)
C(51)-C(52)	1.359(12)	C(52)-C(53)	1.481(12)	N(1)-C(41)-C(42)	115.9(4)	C(41)-C(42)-C(43)	109.2(5)
C(61)-C(62)	1.335(12)	C(62)-C(63)	1.462(11)	C(51)-N(2)-C(61)	108.2(5)	C(51)-N(2)-C(71)	109.9(5)
C(71)-C(72)	1.343(15)	C(72)-C73)	1.476(14)	C(61)-N(2)-C(71)	108.3(6)	C(51)-N(2)-C(81)	109.6(6)
C(81)-C(82)	1.381(13)	C(82)-C(83)	1.473(12)	C(61)-N(2)-C(81)	110.8(6)	C(71)-N(2)-C(81)	109.9(5)
				N(2)-C(51)-C(52)	122.9(8)	C(51)-C(52)-C(53)	121.6(9)
				N(2)-C(61)-C(62)	126.6(7)	C(61)-C(62)-C(63)	120.0(8)
				N(2)-C(71)-C(72)	124.5(7)	C(71)-C(72)-C(73)	119.8(8)
				N(2)-C(81)-C(82)	121.6(7)	C(81)-C(82)-C(83)	120.8(8)

Table 5. Bond lengths (Å) and angles (°) for the non-hydrogen atoms of $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ (2), with estimated standard deviations in parentheses. Primes denote atoms generated by the symmetry operation $-x, y, \frac{1}{2} - z$

Mo···Cu	2.632(1)			S(1)-Mo-S(2)	107.1(1)	S(1)-Mo-S(1′)	109.5(1)
Mo-S(1)	2.210(2)	Mo-S(2)	2.201(2)	S(2)-Mo-S(1′)	111.7(1)	S(2)-Mo-S(2′)	109.7(1)
Cu-S(1)	2.211(2)	Cu-S(2)	2.213(2)	S(1)-Cu-S(2)	106.6(1)	S(1)-Cu-S(3)	132.4(1)
Cu-S(3)	2.171(2)	S(3)-C(1)	1.755(5)	S(2)-Cu-S(3)	120.8(1)	Mo-S(1)-Cu	73.1(1)
C(1)-C(2)	1.383(8)	C(1)-C(6)	1.387(7)	Mo-S(2)-Cu	73.2(1)	Cu-S(3)-C(1)	110.5(2)
C(2)-C(3)	1.371(9)	C(3)-C(4)	1.362(10)	S(3)-C(1)-C(2)	124.1(4)	S(3)-C(1)-C(6)	119.1(4)
C(4)-C(5)	1.354(12)	C(5)-C(6)	1.380(11)	C(2)-C(1)-C(6)	116.7(5)	C(1)-C(2)-C(3)	121.7(5)
N-C(11)	1.506(7)	N-C(21)	1.521(6)	C(2)-C(3)-C(4)	120.1(6)	C(3)-C(4)-C(5)	120.0(7)
N-C(31)	1.517(6)	N-C(41)	1.516(6)	C(4)-C(5)-C(6)	120.2(6)	C(1)-C(6)-C(5)	121.3(6)
C(11)-C(12)	1.512(7)	C(12)-C(13)	1.498(12)	C(11)-N-C(21)	112.1(3)	C(11)-N-C(31)	106.3(4)
C(21)-C(22)	1.516(6)	C(22)-C(23)	1.529(8)	C(21)-N-C(31)	110.3(3)	C(11)-N-C(41)	111.8(4)
C(31)-C(32)	1.500(9)	C(32)-C(33)	1.523(8)	C(21)-N-C(41)	104.6(4)	C(31)-N-C(41)	111.7(3)
C(41)-C(42)	1.535(8)	C(42)-C(43)	1.488(9)	N-C(11)-C(12)	116.2(5)	C(11)-C(12)-C(13)	109.8(6)
				N-C(21)-C(22)	115.3(4)	C(21)-C(22)-C(23)	109.8(5)
				N-C(31)-C(32)	116.4(5)	C(31)-C(32)-C(33)	108.8(6)
				N-C(41)-C(42)	114.0(5)	C(41)-C(42)-C(43)	110.3(6)

on the same side of the anion as the phenyl group is significantly greater [131.5(1) and 132.4(1)°] than the corresponding angle [121.2(1) and 120.8(1)°] opposite to the phenyl group. Presumably this is because of the unfavourable steric interactions between the phenyl group and the MoS_2Cu core introduced by the Cu-S-Ph angle of 111°. These steric interactions are also manifest in the S(3)-C(1)-C(2) angle [124.1(5) and 124.1(4)°], which is significantly greater than the S(3)-C(1)-C(6) angle [118.3(5) and 119.1(4)°]. Also, in $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$, the Cu-S(Mo) distances are significantly different, with that [Cu-S(1) = 2.198(2) Å] on the same side of the structure as the phenyl group being shorter than that [Cu-S(2) = 2.224(2) Å] on the other side of the anion; the average of these two distances (2.211 Å) is the same as that [2.212(2) Å] observed for $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$. These Cu-S(Mo) distances are not significantly different from those reported for $[NPr^n_4]_2[(NC)CuS_2MoS_4]$ [2.207(14) Å],[6] $[PPh_4]_2[(NC)CuS_2MoS_2]$ [2.215(2) Å],[7] and the three-co-ordinate copper in $[(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)]$ [2.220(8) Å].[9]

The bidentate co-ordination of copper(I) by $[MoS_4]^{2-}$ and the dimensions of the MoS_4 groups observed here are consistent with the results of previous studies. Structural studies relevant to (1) include: $[NPr^n_4]_2[(NC)CuS_2MoS_2]$,[6] $[PPh_4]_2[(NC)CuS_2MoS_2]$,[7] $[N(PPh_3)_2]_2[NEt_4][Fe(S_2MoS_2)_2]$,[33] $[NEt_4]_2[(PhS)_2FeS_2MoS_2]$,[30,31] and $[PPh_4]_2[Ni(S_2MoS_2)_2]$.[4] The structural characterizations of $[(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)]$ and its Ag analogue,[9] $[NMe_4]_2[\{(NC)Cu\}_2S_2MoS_2]$,[7] and $[PPh_4]_2[Cl_2FeS_2MoS_2FeCl_2]$ [34] have special relevance to (2). The anion of (1) involves Mo-S(Cu) bonds [2.221(9) Å] which are longer and Mo-S(terminal) bonds [2.162(6) Å] which are shorter than the Mo-S(terminal) bonds (2.178 Å) reported [1] for $[MoS_4]^{2-}$. The sense of this radial polarisation of the MoS_4 group is normal for single bidentate co-ordination; the actual Mo-S distances for $[(PhS)CuS_2MoS_2]^{2-}$ and their difference [Δ(Mo-S) = 0.06 Å] compare closely with values reported for $[(NC)CuS_2MoS_2]^{2-}$ [6,7] [Δ(Mo-S) = 0.08 Å]. When MoS_4 functions as a bidentate ligand to two metal centres (M), to give an approximately linear M-Mo-M array, all the Mo-S bonds are virtually equal in length and slightly longer than in $[MoS_4]^{2-}$. Thus, in $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ the four Mo-S bonds

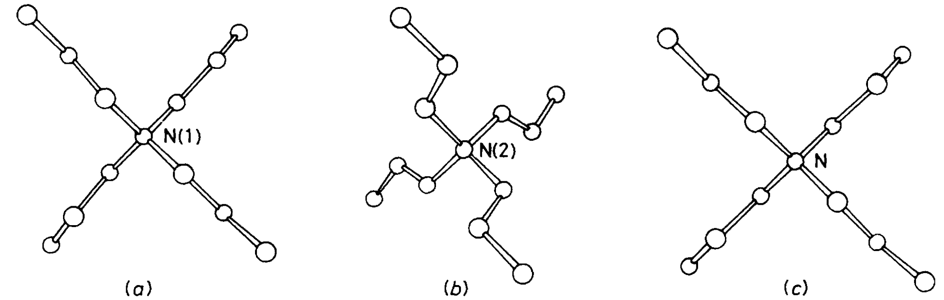

Figure 3. Structure of cations in $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ (*a*) and (*b*) and $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ (*c*)

Table 6. Molybdenum-95 n.m.r. data [a] for $[MoS_4]^{2-}$ and some of its copper(I) complexes

Compound	Solvent [b]	δ/p.p.m.[c]	$\Delta\nu_{\frac{1}{2}}$/Hz
$[NH_4]_2[MoS_4]$	$HC(O)N(CH_3)_2-(CD_3)_2SO$	2 193.8 ± 0.2	9
$[NPr^n_4][CuMoS_4]$	$HC(O)N(CH_3)_2-(CD_3)_2SO$	1 669.7 ± 0.9	40
$[NPr^n_4]_2[(PhS)CuS_2MoS_2]$	CH_3CN-CD_3CN	1 902.5 ± 0.5	50
$[NPr^n_4]_2[(NC)CuS_2MoS_2]$	CH_3CN-CD_3CN	1 863.8 ± 1.0	33
$[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$	CH_3CN-CD_3CN	1 699.8 ± 2.0	630
$[NPr^n_4]_2[(NC)CuS_2MoS_2Cu(CN)]$	CH_3CN-CD_3CN	1 616.4 ± 2.0	245

[a] Recorded at ambient temperature. [b] Containing *ca.* 25% of the deuteriated compound. [c] Referenced to $Na_2[MoO_4]$ in D_2O at 0 p.p.m.

are effectively equivalent and 2.206(6) Å in length *cf.* the values of 2.208(3), and 2.204(5) Å in $[(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)]$ [9] and $[PPh_4]_2[Cl_2FeS_2MoS_2FeCl_2]$,[34] respectively. The angular distortions from tetrahedral geometry at the molybdenum are slight, the most significant being the small reductions of the S–Mo–S angle(s) in the chelate ring, from 109.5° to 106.7(1) and 107.1(1)°, as observed in the majority of other structures [4,6,29,30] involving a bidentate MoS_4 group.

Complexes (1) and (2) involve short Cu · · · Mo distances [2.636(1) Å and 2.632(1) Å see Tables 5 and 6], essentially the same as observed for $[(NC)CuS_2MoS_2]^{2-}$ [2.627(3) Å] [6,7] and for the three-co-ordinate copper in $[(Ph_3P)_2CuS_2MoS_2Cu(PPh_3)]$ [2.642(3) Å].[9] These values, together with the $Cu^I \longrightarrow Mo^{VI}$ charge delocalisation tentatively suggested above, could be taken as indicative of a direct metal–metal bonding interaction. However, no clear evidence to support such a claim has been obtained from the spectroscopic studies accomplished for these complexes.

The dimensions of the benzene rings in these complexes are unexceptional. The cation dimensions are imprecise because of the rather large thermal vibrations. It is interesting, though, that (Figure 3) the cation containing N(1) of $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ and the cation (containing N) of $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ have a ' stretched-out ' conformation, whereas the other cation [containing N(2)] of the former compound has a ' windmill ' appearance. The approximate symmetries are D_{2d} ($\bar{4}2m$) and $S_4(\bar{4})$, respectively, just like the cations in $[NEt_4]_2[S_2OMoS_2MoOS_2]$.[35]

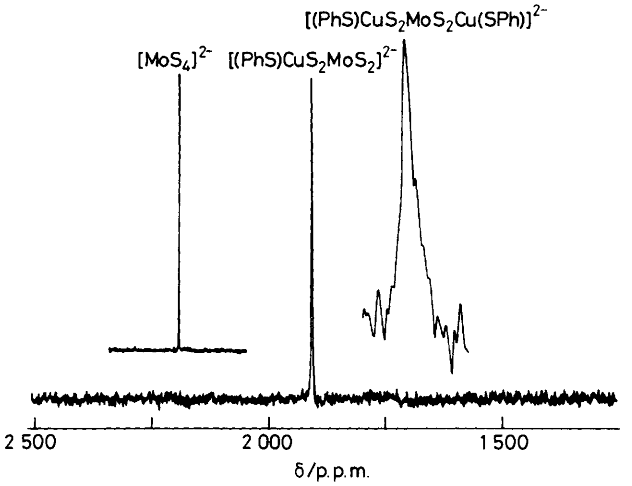

Figure 4. ^{95}Mo n.m.r. spectra of $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ in CH_3CN-CD_3CN, with those of $[NH_4]_2[MoS_4]$ in $HC(O)NMe_2-(CD_3)_2SO$ and $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ in CH_3CN-CD_3CN included for comparison

The ^{95}Mo n.m.r. spectra of the complexes reported herein and some related systems have been recorded and these results are summarised in Table 6. The data for $[MoS_4]^{2-}$, $[(NC)CuS_2MoS_2]^{2-}$, and $[(NC)CuS_2MoS_2Cu(CN)]^{2-}$ are in agreement with the results of previous studies.[6,8] As for the cyanocopper(I) derivatives, the corresponding benzenethiolatocopper(I) complexes exhibit ^{95}Mo resonances more ' shielded ' than $[MoS_4]^{2-}$, the upfield displacement from the $[MoS_4]^{2-}$ position and the linewidth of the resonance being significantly greater for the biscopper(I) complex, as compared to the monocopper(I) complex. The ^{95}Mo n.m.r. data indicate that all of the materials dissolve to give, essentially, a single molybdenum-containing complex and thus (Figure 4) show clearly that the position of the equilibrium (i) lies essentially to the left.

$$2[(PhS)CuS_2MoS_2]^{2-} \rightleftharpoons [(PhS)CuS_2MoS_2Cu(SPh)]^{2-} + [MoS_4]^{2-} \quad \text{(i)}$$

Proton n.m.r. spectra of the title complexes and $[NPr^n_4]_2[(4-MeC_6H_6S)CuS_2MoS_2]$ have been recorded in $(CD_3)_2SO$ at ambient temperatures, at 60, 90, and 300 MHz and the 300 MHz data have been used to compile Table 7. The spectra are as expected and the proposed assignment is confirmed by the comparison of the spectra for $[(PhS)CuS_2MoS_2]^{2-}$ and $[(4-MeC_6H_4S)CuS_2MoS_2]^{2-}$. The major perturbation of the resonances from $[PhS]^-$ is the downfield

Table 7. 300 MHz ^1H n.m.r. data[a] for $[(RS)CuS_2MoS_2]^{2-}$ (R = Ph or $4-MeC_6H_4$) and $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$

Species	δ/p.p.m.[b]	Relative intensity	Apparent multiplicity[c]	J/Hz	Assignment
$[PhS]^-$ [d]	7.05	1.9	1 :1 (d)	7.2	*ortho*
	6.65	2.2	1 :2 :1 (t)	7.5	*meta*
	6.21	1.0	1 :2 :1 (t)	7.5	*para*
$[(PhS)CuS_2MoS_2]^{2-}$	7.59	1.9	1 :1 (d)	7.5	*ortho*
	6.88	2.0	1 :2 :1 (t)	7.5	*meta*
	6.68	1.0	1 :2 :1 (t)	7.5	*para*
$[(4-MeC_6H_4S)CuS_2MoS_2]^{2-}$ [e]	7.47	1.9	1 :1 (d)	8.0	*ortho*
	6.70	1.9	1 :1 (d)	8.0	*meta*
	2.10	3.0	(s)	—	$4-CH_3$
$[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ [e]	7.62	1.9	1 :1 (d)	8.0	*ortho*
	6.94	1.9	1 :2 :1 (t)	7.5	*meta*
	6.75	1.0	1 :2 :1 (t)	7.5	*para*

[a] Recorded in $(CD_3)_2SO$ at *ca.* 25 °C. [b] Referenced to hexamethyldisilane at 0 p.p.m. [c] s = Singlet, d = doublet, t = triplet. [d] As K[PhS]. [e] As $[NPr^n_4]^+$ salts; the ^1H n.m.r. spectra of the cations were as expected.

Table 8. Ultraviolet-visible absorption bands for $[(PhS)CuS_2MoS_2]^{2-}$, $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$, and related species *

Compound	$\lambda_{max.}$/nm (ε × 10^{-3}/dm^3 mol^{-1} cm^{-1})
$[NEt_4]_2[MoS_4]$	471 (14.89)
$[NPr^n_4]_2[(4-MeC_6H_4S)CuS_2MoS_2]$	477 (6.70), 348 (sh), 327 (17.69), 285 (24.53), 245 (sh)
$[NPr^n_4]_2[(PhS)CuS_2MoS_2]$	480 (7.25), 350 (sh), 328 (19.68), 286 (26.58), 240 (sh)
$[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$	495 (5.20), 370 (sh), 342 (24.29), 284 (38.21), 245 (sh)

* Recorded in CH_3CN at ambient temperature.

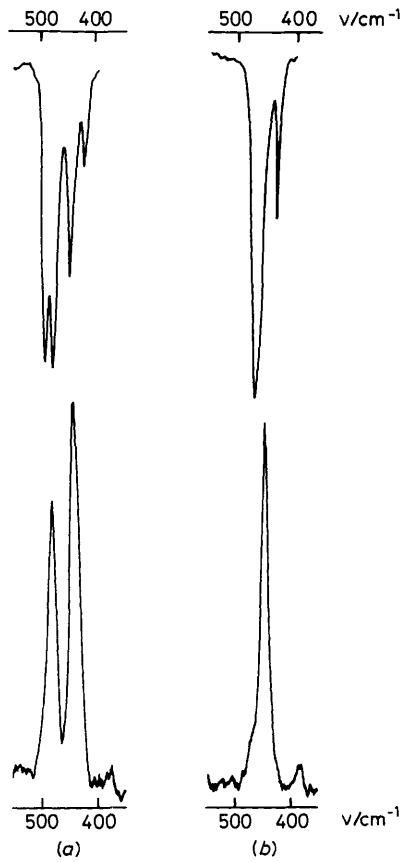

Figure 5. Infrared (upper) and Raman (lower) spectra of (*a*) $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ and (*b*) $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$

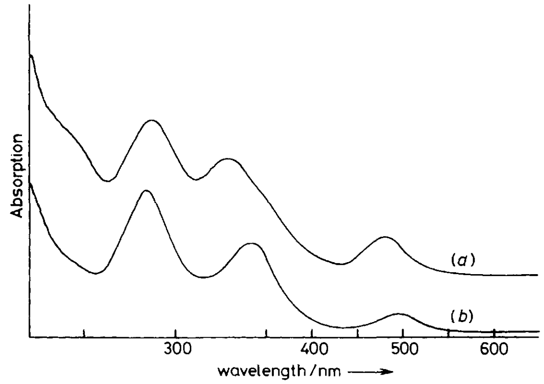

Figure 6. U.v.-visible spectra of (*a*) $[NPr^n_4]_2[(PhS)CuS_2MoS_2]$ and (*b*) $[NPr^n_4]_2[(PhS)CuS_2MoS_2Cu(SPh)]$ in MeCN at ambient temperature

shift of the *ortho* protons, by *ca.* 0.5 p.p.m. This we take to be a consequence of the co-ordination to copper; the ^1H n.m.r. spectra provide no evidence for any paramagnetism of the complexes and the resonances for $[(PhS)CuS_2MoS_2]^{2-}$ show no dependence on temperature from 24 to 80 °C. The data obtained are consistent with free rotation, on the ^1H n.m.r. time-scale, of the aromatic groups about the C–S (and perhaps Cu–S) bond.

The vibrational spectra of $[(PhS)CuS_2MoS_2]^{2-}$ and $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ reflect the different symmetries of the MoS_4 moiety (Figure 5). In the D_{2d} symmetry of $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$, the ν(Mo–S) stretching modes group as a_1 (Raman), b_2 (i.r., Raman), and *e* (i.r., Raman) and the spectra of Figure 5(*b*) are assigned as follows. The intense Raman feature at 450 cm^{-1} is attributed to the a_1 mode and the b_2 and *e* modes are considered to be responsible for the infrared envelope centred at 470 cm^{-1} (possibly the *e* mode gives rise to the main band with a shoulder evident at *ca.* 462 cm^{-1} being due to the b_2 mode). Thiolate vibrations are considered to be responsible for the sharp band at 434 cm^{-1} and a shoulder at *ca.* 477 cm^{-1} of the infrared spectrum of Figure 5(*b*). In the C_{2v} symmetry of $[(PhS)CuS_2MoS_2]^{2-}$, the ν(Mo–S) stretching modes group as $2a_1$, b_1, and b_2, all of which are Raman and infrared active. With reference to the structure of this anion, these modes may be subdivided as the symmetric (a_1) and asymmetric (b_1 or b_2) stretching modes of the terminal and co-ordinated MoS_2 moieties; the bond lengths suggest that the former would have a higher frequency than the latter. Therefore, the Raman bands at 480 and 443 cm^{-1} are attributed primarily to the a_1 modes of the terminal and co-ordinated MoS_2 groups, respectively, these modes being manifest in the infrared spectrum as the band at 479 cm^{-1} and the shoulder at *ca.* 440 cm^{-1}. The infrared bands at 491 and 450 cm^{-1} are attributed primarily to the b_1 and b_2 modes of the terminal and co-ordinated MoS_2 groups, respectively. Vibrations of the thiolate group are considered to be responsible for the infrared band at 427 cm^{-1} and another vibration is probably obscured under the envelope of the two absorptions at 491 and 479 cm^{-1}.

The u.v.-visible spectra of $[(PhS)CuS_2MoS_2]^{2-}$ and $[(PhS)CuS_2MoS_2Cu(SPh)]^{2-}$ are shown in Figure 6. The three principal features are attributed to the charge-transfer transitions of the MoS_4 moiety,[1] perturbed (*i.e.* red-shifted) by co-ordination to one or two (PhS)Cu groups, with no splittings evident due to the consequent lowering of symmetry. The additional shoulders evident at *ca.* 350 and 240 nm are tentatively assigned to S ⟶ Cu charge-transfer transitions, since $[Cu(SPh)_3]^{2-}$ has absorptions near to these energies.[23]

Acknowledgements

We thank the S.E.R.C. for the provision of a CASE studentship (to J. R. N.), the Verband der Chemischen Industrie for financial support (to W. C.), Dr. C. F. Mills for stimulating discussions, Dr. B. E. Mann and the S.E.R.C. n.m.r. service at Sheffield for recording the ^{95}Mo n.m.r. spectra, and Dr. A. G. Wedd for constructive advice and the release of information prior to publication.

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Received 12*th July* 1982; *Paper* 2/1182