Penta- and Hexa-nuclear Ruthenium μ-2-Pyridyl Complexes†

Kenneth I. Hardcastle,*[a] **Bruce R. Cockerton,**[b] **Antony J. Deeming***[b] **and Manzurul Karim**[b]
[a] *Department of Chemistry, California State University Northridge, 18111 Nordhoff Street, Northridge, CA 91330, USA*
[b] *Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK*

The ruthenium(II) pyridine-2-thionato (pyS) complex $[Ru(pyS)_2(CO)_2]$ **1** reacts with $[Ru_3(CO)_{12}]$ in a sealed glass tube under vacuum to give the chain compounds $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2** (38%) and $[Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{12}]$ **3** (23%) (C_5H_4N = 2-pyridyl). The crystal structure of **2** shows it to contain three Ru_2 units linked into a chain by tetrahedral μ_4-sulfur atom bridges and with the terminal Ru_2 units co-ordinated to $\mu\text{-}C_5H_4N$ ligands. Isomerism in compounds **2** and **3** results from the different geometries of attachment of the $\mu\text{-}C_5H_4N$ ligands. If the reaction of **1** with $[Ru_3(CO)_{12}]$ is alternatively carried out in refluxing xylene under nitrogen so that CO can escape there is considerable decomposition but a compound with lower CO content, $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4**, is formed in low yield (15%). The crystal structure shows that cluster **4** contains five Ru–Ru bonds within a Ru_5S_2 pentagonal bipyramidal unit with two axial Ru atoms linked by non-disordered $\mu\text{-}C_5H_4N$ bridges to Ru atoms in the equatorial plane. The μ_4-S atoms are pyramidal rather than tetrahedral.

The monomeric compound $[Ru(pyS)_2(CO)_2]$ **1** (pyS = pyridine-2-thionate, C_5H_4NS) can be synthesised in high yields from either $[Ru_3(CO)_{12}]$ or $RuCl_3\cdot 3H_2O$ as we have described previously.[1] Compound **1** is a *cis*-dicarbonyl octahedral ruthenium(II) species with equivalent chelating pyS ligands, analogous to the osmium complex for which the structure is known.[2] In our previous work on mixed tetranuclear rhenium–ruthenium complexes[3] the compound $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2** (C_5H_4N = 2-pyridyl) was isolated in trace amounts from the reaction between $[Ru_3(CO)_{12}]$ and $[Re_2(pyS)_2(CO)_6]$. Expecting that compound **2** could be effectively synthesised directly from $[Ru_3(CO)_{12}]$ and **1**, we carried out this reaction and obtained chain or cluster compounds with nuclearities of four to six depending upon the conditions. Each complex contains μ_4-sulfido and μ-2-pyridyl ligands formed by cleavage of a C–S bond of a pyS ligand. These compounds and isomerism resulting from the different orientations of the 2-pyridyl ligands are the subject of this paper.

Results and Discussion

Syntheses.—Compound **1** and $[Ru_3(CO)_{12}]$ were heated in light petroleum (b.p. 120–160 °C) solution at 150 °C for 18 h in an evacuated sealed glass tube. The resulting mixture was separated by successive TLC treatments into two major components: yellow crystals of $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2** (38%) and yellow crystals of $[Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{12}]$ **3** (23%). These samples were characterised by elemental analysis, mass, IR, and ^1H NMR spectroscopy (Tables 1 and 2) and in the case of compound **2** by X-ray diffraction (XRD).

Compounds **2** and **3** have a CO/Ru ratio of 3:1, but if the thermal reaction is carried out in an open vessel at atmospheric pressure so that CO can escape a product with CO/Ru ratio of only 2.2:1 was obtained. Thus, equimolar amounts of compound **1** and $[Ru_3(CO)_{12}]$ were heated under reflux in *m*-xylene for 30 min under nitrogen to give, after TLC separation, ruby-red crystals of $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4** which was characterised by elemental analysis, infrared, mass, ^1H NMR spectroscopy and X-ray diffraction. Most of the material did not elute during TLC separation and remains uncharacterised. The synthetic results are summarised in Scheme 1.

Table 1 IR data

Compound	$\nu(CO)^a/cm^{-1}$
1 $[Ru(pyS)_2(CO)_2]$	2046vs, 1988vs
2 $[Ru_6S_2(C_5H_4N)_2(CO)_{18}]^b$	2076s, 2066s, 2051s, 2046s, 2013s, 2007s, 1997s, 1990s, 1975m, 1956w
3 $[Ru_4S(C_5H_4N)_2(CO)_{12}]^b$	2083, 2065, 2046, 2009, 1993(br), 1976w
4 $[Ru_5S_2(C_5H_4N)_2(CO)_{11}]$	2060m, 2073vs, 2016vs, 2013(sh), 2004m, 1989s, 1975s, 1963m, 1961(sh)

[a] Recorded in cyclohexane solution. [b] Mixture of isomers.

Table 2 Proton NMR data

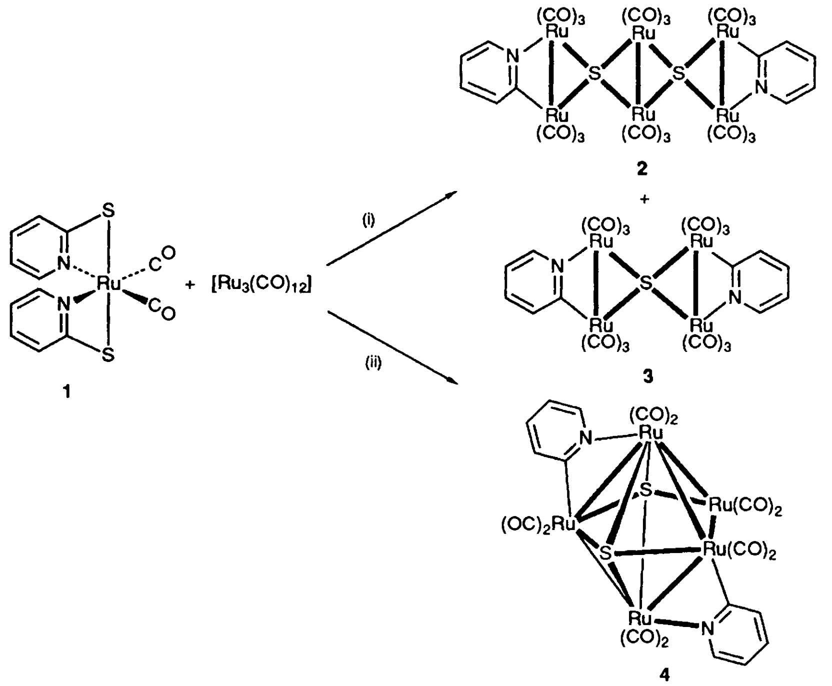
Compound	δ*
1	8.13 (ddd, J = 5.4, 1.3, H^6), 7.38 (ddd, J = 8.3, 7.3, 1.4, H^4), 6.86 (ddd, J = 8.3, 1.0, H^3), 6.75 (ddd, J = 8.5, 5.6, 1.3, H^5)
2	7.85 (ddd, J = 5.5, 2.5, 1.6, H^6), 7.77 (ddd, J = 5.5, $H^{6'}$), 7.75 (ddd, J = 5.6, $H^{6''}$), 7.30–7.18 (m, 3 H^4, 3 H^3), 6.89–6.83 (m, 3 H^5)
3	Isomer **a**: 7.80 (ddd, J = 5.5, 1.6, 0.9, H^6), 7.55 (ddd, J = 5.5, 1.6, 0.9, $H^{6'}$), 7.28–7.19 (m, 2 H^4, H^3), 7.03 (ddd, J = 7.7, 1.5, 0.9, H^3), 6.87–6.79 (m, 2 H^5) Isomer **b**: 7.58 (ddd, J = 5.5, H^6), 7.28–7.19 (m, H^4, H^3), 6.87–6.79 (m, H^5) Isomer **c**: 7.82 (ddd, J = 5.5, H^6), 7.28–7.19 (m, H^4), 7.00 (ddd, J = 7.7, H^3), 6.87–6.79 (m, H^5)
4	8.02 (ddd, J = 8.0, 1.0, H^6), 7.62 (ddd, J = 5.6, 1.7, 0.9, H^6), 7.49–7.40 (m, 2 H^4), 7.29–7.1 (m, 2 H^5), 6.90 (ddd, J = 5.6, 1.7, 0.9, H^3), 6.62 (ddd, J = 8.4, 6.3, 1.5, H^3)

* Recorded in $CDCl_3$ at 400 MHz; J in Hz.

Characterisation.—For all ruthenium compounds **2**–**4** there is the possibility of isomers arising from different orientations

---

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 (*i*) Light petroleum, 150 °C, Carius-tube; (*ii*) Xylene, reflux

Table 3 Selected bond lengths (Å) and angles (°) for the compound $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2**

Ru(2)–Ru(1)	2.722(1)	Ru(4)–Ru(3)	2.714(1)
Ru(5)–Ru(6)	2.713(2)	Ru(2)–S(1)	2.398(3)
Ru(1)–S(1)	2.409(3)	Ru(3)–S(1)	2.407(3)
Ru(4)–S(1)	2.403(3)	Ru(4)–S(2)	2.406(3)
Ru(3)–S(2)	2.382(3)	Ru(5)–S(2)	2.387(3)
Ru(6)–S(2)	2.390(3)	Ru(2)–N(1)	2.09(1)
Ru(1)–C(1)	2.097(9)	Ru(5)–N(2)	2.09(1)
Ru(6)–C(6)	2.12(1)		
Ru(1)–S(1)–Ru(2)	69.0(1)	Ru(3)–S(1)–Ru(4)	68.7(1)
Ru(3)–S(2)–Ru(4)	69.1(1)	Ru(5)–S(2)–Ru(6)	69.2(3)
Ru(1)–S(1)–Ru(3)	146.0(1)	Ru(1)–S(1)–Ru(4)	130.2(1)
Ru(2)–S(1)–Ru(3)	126.8(1)	Ru(2)–S(1)–Ru(4)	126.8(1)
Ru(3)–S(2)–Ru(5)	131.1(1)	Ru(3)–S(2)–Ru(6)	132.7(1)
Ru(4)–S(2)–Ru(5)	124.0(1)	Ru(4)–S(2)–Ru(6)	142.4(1)
Ru(1)–Ru(2)–S(1)	55.7(1)	Ru(2)–Ru(1)–S(1)	55.3(1)
Ru(3)–Ru(4)–S(1)	55.7(1)	Ru(4)–Ru(3)–S(1)	55.6(1)
Ru(3)–Ru(4)–S(2)	55.1(1)	Ru(4)–Ru(3)–S(2)	55.9(1)
Ru(5)–Ru(6)–S(2)	55.3(1)	Ru(6)–Ru(5)–S(2)	55.5(1)
Ru(1)–Ru(2)–N(1)	71.2(2)	Ru(2)–Ru(1)–C(1)	71.3(3)
Ru(1)–C(1)–N(1)	108.4(7)	Ru(2)–N(1)–C(1)	109.0(7)
Ru(6)–Ru(5)–N(2)	71.0(3)	Ru(5)–Ru(6)–C(6)	71.2(3)
Ru(6)–C(6)–N(2)	107.5(7)	Ru(5)–N(2)–C(6)	110.2(7)

of the 2-pyridyl ligands with respect to the metal frameworks. Isomers are indeed observed for compounds **2** and **3** but not for **4**. Generally ^1H NMR spectra of this ligand system are easily analysed since four well separated multiplets are observed for each C_5H_4N ligand, the most obvious feature being the H^6 signal at highest δ value. This resonance normally appears as a fairly narrow doublet [$J(H^5H^6)$ = *ca.* 5.5 Hz] with further small couplings to the H^4 and H^3 protons and its chemical shift is most sensitive to the environment of the ligand. We have examined the isomers formed for these compounds by a combination of NMR and XRD methods.

The parent molecular ion in the mass spectrum of compound **2** corresponded to $[Ru_6(\mu_4\text{-}S)_2(\mu_2\text{-}C_5H_4N)_2(CO)_{18}]^+$ and analytical data were also consistent with this formulation. The single-crystal structure of compound **2** was determined for a crystal selected from those grown by slow diffusion of solvents in a layered dichloromethane–methanol mixture. The molecular structure is shown in Fig. 1 and selected bond lengths and angles are in Table 3. Compound **2** is electron precise with three Ru–Ru bonds. The two μ_4-S atoms are approximately tetrahedral and act as six-electron donors linking the three metal–metal bonded Ru_2 units. Because the tricarbonyl units are facial, the Ru_2CN and Ru_2S rings are close to orthogonal and the $Ru_2SRu_2SRu_2$ chain is therefore twisted. An obvious source of disorder is the orientations of the 2-pyridyl ligands. Fig. 2 shows three possible isomers based on this crystal structure and differing only in C_5H_4N orientations; isomers **2a** and **2b** are of C_2 symmetry and have equivalent ligands related by the two-fold rotation axis whereas **2c** is of C_1 symmetry with non-equivalent ligands. Experimentally a knowledge of the orientation of the C_5H_4N ligands in the crystal depends upon the relative positioning of the C and N atoms bonded to ruthenium. The best refinement of the structure was when orientational disorder of the 2-pyridyl ligands was included in the model. Allowing the relative populations of C and N atoms to refine gave a best solution with a fractional population of 0.7(1) for atoms N(1) and C(1) in the positions illustrated in Fig. 1 together with a 0.3(1) population of the reverse orientation of these atoms, labelled as N(1a) and C(1a) when reversed. There is a closely similar situation for the other pyridyl ring for which the best refinement gave atoms N(2) and C(6) with a fractional population of 0.7(1) with the reversely orientated atoms N(2a) and C(6a) having populations of 0.3(1). Overall therefore there is an approximately 70% preference for the N atoms to be in the positions occupied by N(1) and N(2) in Fig. 1. This observed crystallographic disorder could be rationalised as resulting from an unequal distribution of all three isomers **2a**–**2c** (Fig. 2) throughout the crystal lattice. A completely statistical distribution of 2-pyridyl orientations would, of course, lead to an isomer ratio of 1:1:2 for the isomers **2a**:**2b**:**2c** and populations of 0.5 for both C and N atoms in each of the metal-bound ligand sites. However, the determined populations of the disordered 2-pyridyl ligands in the crystal must favour isomer **2b** over **2a**.

The ^1H NMR spectrum of $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2** shows a complicated set of overlapping multiplets for protons

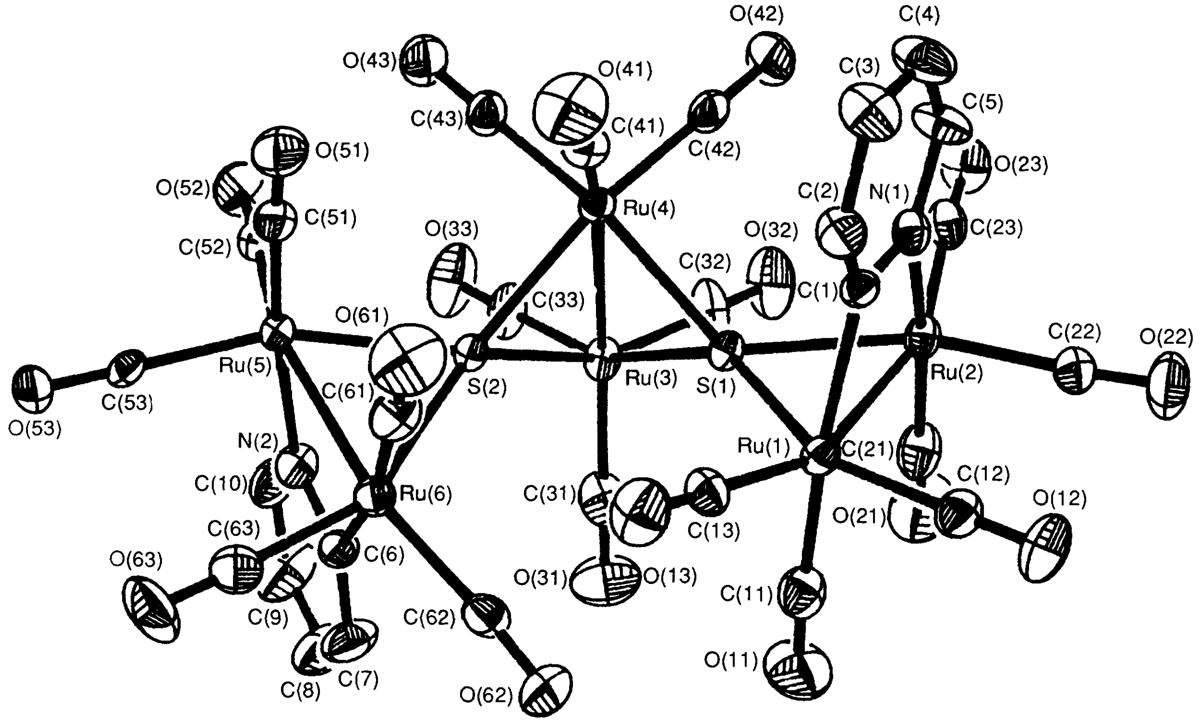


Fig. 1 Molecular structure of the compound $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2** showing the predominant orientations of the C_5H_4N ligands (0.7 ± 0.1). Replacing N(1), C(1), N(2) and C(6) by C(1a), N(1a), C(6a) and N(2a) respectively generates the minor orientational isomer (0.3 ± 0.1)

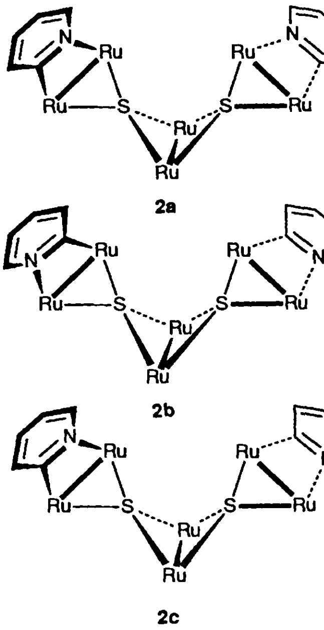


Fig. 2 Isomers of compound **2** showing all the possible orientations of the C_5H_4N ligands (CO ligands are omitted)

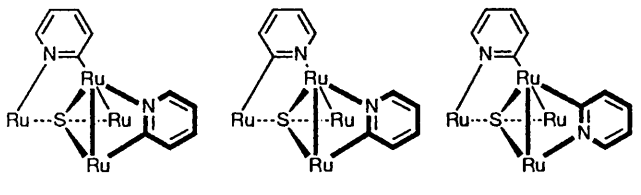
Table 4 Selected bond lengths (Å) and angles (°) for the compound $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4**

Ru(1)–Ru(2)	2.920(1)	Ru(1)–Ru(3)	2.841(1)
Ru(2)–Ru(4)	3.019(1)	Ru(2)–Ru(5)	2.808(1)
Ru(3)–Ru(4)	2.838(1)	Ru(3)–Ru(5)	2.943(1)
Ru(4)–Ru(5)	2.780(1)	Ru(1)–S(1)	2.415(2)
Ru(1)–S(2)	2.421(2)	Ru(2)–S(1)	2.519(2)
Ru(2)–S(2)	2.500(2)	Ru(3)–S(1)	2.427(1)
Ru(3)–S(2)	2.487(2)	Ru(4)–S(2)	2.428(2)
Ru(5)–S(1)	2.396(2)	Ru(1)–C(1a)	2.034(7)
Ru(2)–N(1a)	2.128(6)	Ru(3)–N(1b)	2.072(5)
Ru(4)–C(1b)	2.010(9)		
Ru(1)–S(1)–Ru(2)	72.55(6)	Ru(1)–S(1)–Ru(3)	71.85(4)
Ru(1)–S(1)–Ru(5)	128.87(7)	Ru(2)–S(1)–Ru(3)	90.33(6)
Ru(2)–S(1)–Ru(5)	69.65(6)	Ru(3)–S(1)–Ru(5)	75.20(5)
Ru(1)–S(2)–Ru(2)	72.78(5)	Ru(1)–S(2)–Ru(3)	70.73(5)
Ru(1)–S(2)–Ru(4)	129.41(8)	Ru(2)–S(2)–Ru(3)	89.39(6)
Ru(2)–S(2)–Ru(4)	75.54(6)	Ru(3)–S(2)–Ru(4)	70.53(5)
Ru(1)–Ru(3)–Ru(5)	97.21(2)	Ru(4)–Ru(3)–Ru(5)	57.43(2)
Ru(2)–Ru(4)–Ru(3)	73.50(2)	Ru(2)–Ru(4)–Ru(5)	57.76(2)
Ru(3)–Ru(4)–Ru(5)	63.18(2)	Ru(2)–Ru(5)–Ru(3)	75.12(2)
Ru(2)–Ru(5)–Ru(4)	65.41(2)		

H^3, H^4 and H^5. However the signals for the H^6 protons were well resolved and indicated a mixture of three isomers in an approximate ratio of 8:3:2. Careful TLC, collecting the upper and lower extremes of the yellow band separately, gave no evidence for even a partial separation; HPLC was also applied but no separation was observed.

Isomers resulting from the orientations of 2-pyridyl ligands have been seen previously. Head-to-head and head-to-tail isomers of the complex $[Os_2(\mu\text{-}C_5H_4N)_2(CO)_6]$ have been separated[4] and the crystal structures of the corresponding compounds from 4-methylpyridine have been determined.[5] More recently isomeric clusters $[Ru_5H(C)(\mu\text{-}C_5H_4N)(CO)_{14}]$ containing different orientations of this ligand have been separated and structurally characterised.[6] Enantiomers of $[Os_3H(\mu\text{-}C_5H_4N)(CO)_{10}]$ differ only in the 2-pyridyl orientation and have been resolved.[7] There is apparently a very large energy barrier to the reorientation of μ-2-pyridyl bridges in all observed cases.

The structure of $[Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{12}]$ **3** illustrated was based on spectra and an analogy with that of **2**. This compound also exhibits isomerism arising from the orientations of the 2-pyridyl ligands but attempts to resolve these isomers by TLC and HPLC were unsuccessful. Three isomers of the compound can be envisaged, **3a**–**3c** (Fig. 3), all of which are chiral. Isomer **3a** has C_1 symmetry but **3b** and **3c** possess C_2 axes relating the two C_5H_4N ligands. Analysis of the H^6 signals in the ^1H NMR spectrum (Fig. 4 and Table 2) indicates that all three isomers are present. The unsymmetrical isomer **3a** contains two different environments for the H^6 proton giving two signals of equal intensity as indicated in Fig. 4. One H^6 signal is observed for each of the C_2 isomers, **3b** and **3c**. This leads to four H^6 signals in total, exactly as observed. For a purely statistical distribution of isomers the population ratio for **3a**, **3b** and **3c** would be 2:1:1. However the observed distribution is approximately 2.5:0.8:1.0 (from ^1H NMR integrations) indicating a small preference for the unsymmetric isomer **3a**. We assign the H^6 signals at δ 7.80 and 7.55 to the unsymmetrical isomer **3a**. Each of the weaker H^6 signals can be assigned to one of the symmetric isomers. We can tentatively assign the signal at higher field (δ 7.58) to **3b** since we believe that each H^6 proton experiences an upfield shift (relative to those in **3c**) due to the magnetic anisotropy of the adjacent C_5H_4N ring. In isomer **3c** there is no such effect since each H^6 proton is on the opposite side of the molecule and well away from the other C_5H_4N ring; the H^6 signal at δ 7.82 is assigned to isomer **3c**. Note that for **3a** one H^6 signal is at high and the other at low δ. A similar argument can be used to assign the H^3 signals which are also separated by 0.2 ppm.



3a **3b** **3c**

Fig. 3 Isomers of compound 3 showing all the possible orientations of the C_5H_4N ligands (CO ligands are omitted)

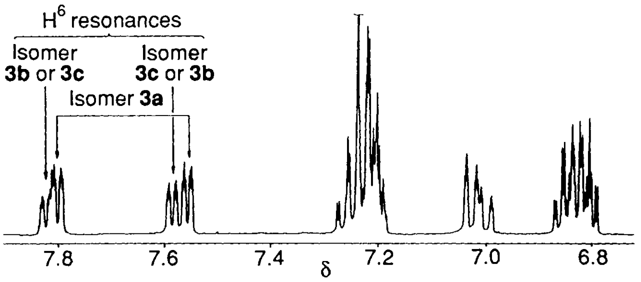


Fig. 4 Proton NMR spectrum of an isomeric mixture of the compound $[Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{12}]$ **3** recorded in $CDCl_3$ at 20 °C at 400 MHz

The highest-mass ion observed in the fast atom bombardment (FAB) mass spectrum of compound **3** is that which corresponds to loss of two CO ligands from the parent complex to give $[Ru_4(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{10}]^+$. Calculated isotopic abundance patterns for this species are entirely consistent with the observed isotopic patterns.

The compound $[Ru_5(\mu_4\text{-}S)(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4** was isolated from a reaction between **1** and $[Ru_3(CO)_{12}]$ carried out in an open vessel (see Experimental section), whereas **2** and **3** were from a reaction in an evacuated sealed tube from which no CO could be lost. These different conditions explain the higher CO:Ru ratio and the higher yields of compounds **2** and **3**.

Analytical data fitted well with the formula $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ and the parent molecular ion was observed in a FAB mass spectrum. The ^1H NMR spectrum (Table 2) showed that there are only two different C_5H_4N environments and that these are equally populated. A crystal structure determination has confirmed that there are two different C_5H_4N ligand environments in the molecule. The molecular structure is shown in Fig. 5 and selected bond lengths and angles are in Table 4. There is only one isomeric form both in solution and in the crystal. The five non-equivalent ruthenium atoms are bonded by seven metal–metal bonds to form what could be described as an Ru_4 butterfly composed of atoms Ru(2) to Ru(5) with the fifth metal atom, Ru(1), bridging the wing-tip atoms Ru(2) and Ru(3). The Ru_5S_2 atoms as a whole form a pentagonal bipyramid. The overall geometry is asymmetric since the two bridging C_5H_4N ligands bridge non-equivalent metal–metal bonded edges: Ru(1)–Ru(2) and Ru(3)–Ru(4). Counting the μ_4-S atoms as four-electron donors and the C_5H_4N ligands as three-electron donors, we would expect there to be seven metal–metal bonds as found. Sulfur atoms are potentially six-electron donors which is achieved when they are tetrahedrally surrounded by four metal atoms as in compounds **2** and **3**. However, a sulfur atom capping a face of three or four metal atoms as in $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4** is a four-electron donor and retains a lone pair pointing

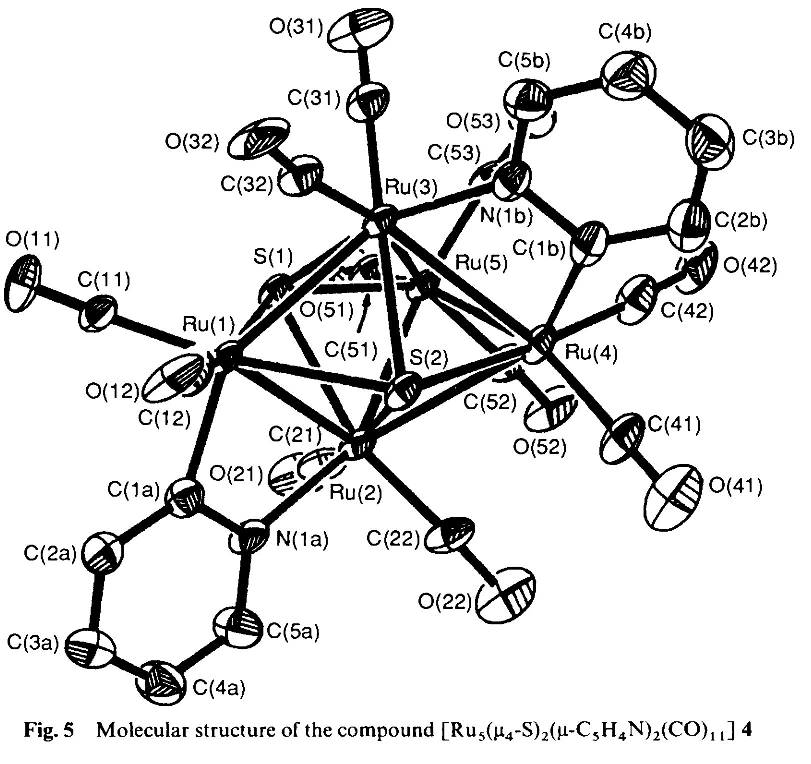


Fig. 5 Molecular structure of the compound $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4**

Table 5 Crystallographic data for compounds $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2** and $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4**[a]

	Compound 2	Compound 4
Formula	$C_{28}H_8N_2O_{18}Ru_6S_2$	$C_{21}H_8N_2O_{11}Ru_5S_2$
M	1330.92	1033.78
Colour	Yellow	Ruby-red
Crystal size/mm	0.25 × 0.22 × 0.05	0.21 × 0.27 × 0.38
Space group	Cc	$P2_1/c$
a/Å	10.329(3)	10.118(3)
b/Å	16.256(5)	14.321(3)
c/Å	24.126(7)	21.541(4)
β/°	90.73(2)	115.52(2)
U/Å^3	4050(2)	2817(1)
D_c/g cm^{-3}	2.18	2.44
μ(Mo-Kα)/cm^{-1}	23.1	27.7
Maximum and minimum relative transmission coefficients	1.000, 0.857	1.000, 0.906
$F(000)$	2520	1952
Diffractometer	Nicolet R3v/m	Enraf-Nonius CAD4
T/°C	23	25
No. orientation reflections, 2θ range/°	30; $6 \leqslant 2\theta \leqslant 24$	23; $11 \leqslant 2\theta \leqslant 15$
Structure solution	Direct methods	Patterson
Total data	7641	5311
Unique data	6113	5155
Reflections used	5346	4188
Parameters refined	505	371
R[b]	0.0420	0.0488
R'[c]	0.0366	0.0649
Weight w	$[\sigma^2(F_o) + 0.000\,245(F_o^2)]^{-1}$	$4F_o^2/[\sigma(F_o)^2]^2$
Maximum shift/e.s.d. in final refinement	0.001	0.01
Largest residual peak/e Å^{-3}	0.9	1.1

[a] Data common to compounds **2** and **4**: molybdenum radiation (λ = 0.710 73 Å); monoclinic; $Z = 4$; scan mode ω–2θ; maximum 2θ for data collection = 50°; intensity data were corrected for decay based on intensities of check reflections, for Lorentz and polarisation effects, and for absorption by azimuthal scan method; rejection criterion $I_o < 1.5\sigma(I_o)$. [b] $R = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

radially away from the centre of the cage. The seven metal–metal bonds are in the range 2.780(1)–3.019(1) Å which can be compared with that of 2.852(1) Å in $[Ru_3(CO)_{12}]$.[8] Four possible isomers of **4** might have been obtained by changing the orientations of the C_5H_4N ligands but only one is observed. The metal-bonded C and N atoms of the C_5H_4N ligands in compounds **2** and **3** are both *trans* to a S atom and the difference between C_5H_4N orientations is only apparent when considering the geometry of the next Ru_2 unit along. However, in cluster **4** the C_5H_4N ligands bridge Ru atoms that are in very different environments and one C_5H_4N orientation is much preferred energetically over the other and hence only one isomer of **4** is found.

The compound $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4** could be regarded as being derived from $[Ru(pyS)_2(CO)_2]$ and $[Ru_4(CO)_9]$ but almost certainly the latter set of atoms is added in stages, perhaps as Ru_2 units. Notably though, both pyS ligands of the mononuclear unit after cleavage remain in the final cluster. Cleavage of a pyS ligand leaves S and C_5H_4N ligands both of which bind strongly to the metal atoms and neither is lost. This was also found for some mixed Re–Ru compounds described elsewhere[3] and seems to be a common feature with this ligand system. However, the compound $[Ru_4S(C_5H_4N)_2(CO)_{12}]$ **3** is exceptional in that one of the sulfur atoms is lost. Note that the derived components of a single pyS ligand donate seven electrons in the final compound **4** and nine electrons in **2** and **3**. The strength and the number of bonds formed between metal atoms and S and C_5H_4N groups and the high number of electrons donated by these ligands facilitates C–S bond cleavage in these systems.

Experimental

Reaction of $[Ru_3(CO)_{12}]$ *with Pyridine-2-thione in Refluxing* m*-Xylene.*—Following a method similar to that described previously,[1] a mixture of $[Ru_3(CO)_{12}]$ (0.200 g, 0.310 mmol) and pyridine-2-thione (0.208 g, 1.19 mmol) in *m*-xylene (50 cm^3) was heated under reflux under nitrogen for 2 h. The solvent was removed under vacuum and the residue (deep yellow) separated by TLC [SiO_2; light petroleum (b.p. < 40 °C)–dichloromethane (1:1 v/v)] to give the complex $[Ru(pyS)_2(CO)_2]$ as yellow crystals (0.317 g, 89%) from a dichloromethane and hexane mixture (Found: C, 38.05; H, 2.25; N, 7.35; S, 16.75. $C_{12}H_8N_2O_2RuS_2$ requires C, 38.2; H, 2.15; N, 7.4; S, 17.0%) and $[Ru(pyS)_2(pySH)(CO)]$ as orange needle-shaped crystals (0.008 g, 2%) from a dichloromethane and hexane mixture (Found: C, 41.25; H, 2.80; N, 8.9; S, 20.85. $C_{16}H_{13}N_3ORuS_3$ requires C, 41.7; H, 2.85; N, 9.1; S, 20.9%).

Thermal Reaction of $[Ru(pyS)_2(CO)_2]$ *with* $[Ru_3(CO)_{12}]$ *at* 150 °C.—The complexes $[Ru(pyS)_2(CO)_2]$ (0.173 g, 0.46 mmol) and $[Ru_3(CO)_{12}]$ (0.491 g, 0.77 mmol) were introduced into a Carius tube and light petroleum (b.p. 120–160 °C) (30 cm^3) was added. Three freeze (liquid nitrogen)–pump–thaw cycles were performed to degass and evacuate the tube which was then sealed under vacuum. The sealed tube and contents were then heated at 150 °C for 18 h. The tube was opened and the solvent was removed under reduced pressure and the residue separated by TLC [SiO_2; light petroleum (b.p. < 40 °C)–dichloromethane (5:1 v/v)] to give three fractions. The middle yellow band (major) was rechromatographed by TLC as above to give the compound $[Ru_6S_2(C_5H_4N)_2(CO)_{18}]$ as a yellow solid (0.233 g, 38%) by slow evaporation of a dichloromethane solution (Found: C, 25.45; H, 0.65; N, 2.1; S, 4.65. $C_{28}H_8N_2O_{18}Ru_6S_2$ requires C, 25.25; H, 0.6; N, 2.1; S, 4.8%) and the compound $[Ru_4S(C_5H_4N)_2(CO)_{12}]$ as a yellow solid (0.096 g, 23%) by slow evaporation of a dichloromethane solution (Found: C, 28.4; H, 1.0; N, 3.0; S, 3.3. $C_{22}H_8N_2O_{12}Ru_4S$ requires C, 28.45; H, 0.95; N, 3.0; S, 3.45%). One green (0.012 g) and one yellow (0.027 g) fraction from the original TLC remain unidentified.

Thermal Reaction of $[Ru(pyS)_2(CO)_2]$ *with* $[Ru_3(CO)_{12}]$ *in* m*-Xylene at* 138 °C.—A mixture of the compounds $[Ru(pyS)_2(CO)_2]$ (0.043 g, 0.09 mmol) and $[Ru_3(CO)_{12}]$ (0.058 g, 0.09

Table 6 Fractional atomic coordinates (× 10^4) for the compound $[Ru_6(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{18}]$ **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(4)	1257	3970(1)	1247	C(22)	3886(13)	3615(8)	3505(5)
Ru(2)	3484(1)	3930(1)	2762(1)	O(22)	4081(12)	3459(6)	3951(4)
Ru(3)	3702(1)	4470(1)	1022(1)	C(23)	2814(13)	5039(8)	2892(5)
Ru(5)	1949(1)	3288(1)	−416(1)	O(23)	2467(10)	5669(6)	2990(4)
Ru(1)	3617(1)	2392(1)	2319(1)	C(31)	5520(16)	4263(9)	898(6)
Ru(6)	3304(1)	2123(1)	151(1)	O(31)	6598(12)	4136(9)	835(6)
S(1)	3130(3)	3622(2)	1800(1)	C(32)	3906(15)	5371(8)	1518(5)
S(2)	2597(3)	3400(2)	534(1)	O(32)	3981(13)	5900(6)	1813(5)
N(1)	1679(9)	3362(6)	2837(3)	C(33)	3421(13)	5199(7)	429(5)
C(1)	1746(9)	2578(6)	2622(4)	O(33)	3204(13)	5642(6)	73(4)
C(2)	690(12)	2092(8)	2629(5)	C(41)	−50(11)	3122(7)	1389(4)
C(3)	−490(13)	2374(8)	2823(5)	O(41)	−813(11)	2646(7)	1432(5)
C(4)	−523(13)	3160(9)	3039(6)	C(42)	721(13)	4752(8)	1798(5)
C(5)	559(11)	3646(8)	3044(6)	O(42)	434(11)	5220(6)	2107(4)
N(2)	3927(10)	3469(6)	−546(4)	C(43)	207(12)	4490(7)	695(5)
C(6)	4622(10)	2875(6)	−288(4)	O(43)	−389(10)	4809(6)	370(4)
C(7)	5919(14)	2844(11)	−355(6)	C(51)	262(13)	2928(8)	−183(5)
C(8)	6562(14)	3421(13)	−656(7)	O(51)	−706(9)	2739(7)	−18(4)
C(9)	5914(14)	4010(12)	−908(7)	C(52)	1431(12)	4367(8)	−670(5)
C(10)	4593(13)	4045(9)	−858(5)	O(52)	1107(12)	4993(6)	−831(4)
C(11)	5399(15)	2402(8)	2109(5)	C(53)	1784(10)	2731(7)	−1101(5)
O(11)	6488(10)	2451(8)	2012(5)	O(53)	1661(8)	2396(6)	−1515(4)
C(12)	3978(12)	1787(8)	2977(5)	C(61)	1856(13)	1562(8)	486(5)
O(12)	4171(11)	1410(6)	3370(4)	O(61)	980(11)	1262(6)	672(5)
C(13)	3101(12)	1452(7)	1880(5)	C(62)	4667(13)	1715(7)	647(5)
O(13)	2766(11)	883(6)	1646(4)	O(62)	5497(13)	1485(6)	904(4)
C(21)	5284(16)	4258(9)	2625(5)	C(63)	3383(14)	1319(8)	−429(6)
O(21)	6280(12)	4476(9)	2568(6)	O(63)	3381(13)	856(6)	−767(4)

Table 7 Fractional atomic coordinates for the compound $[Ru_5(\mu_4\text{-}S)_2(\mu\text{-}C_5H_4N)_2(CO)_{11}]$ **4**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru(1)	0.497 54(6)	0.204 31(4)	−0.037 04(3)	C(1b)	0.800 3(9)	0.208 2(6)	0.221 2(4)
Ru(2)	0.324 29(6)	0.234 46(4)	0.040 07(3)	C(2a)	0.248(1)	0.086 0(6)	−0.145 9(4)
Ru(3)	0.691 98(5)	0.292 28(4)	0.087 05(3)	C(2b)	0.899(1)	0.172 4(7)	0.285 2(5)
Ru(4)	0.581 97(6)	0.225 89(4)	0.179 86(3)	C(3a)	0.110(1)	0.048 0(7)	−0.169 4(5)
Ru(5)	0.469 08(6)	0.394 02(4)	0.113 84(3)	C(3b)	1.048(1)	0.170 2(7)	0.302 9(5)
S(1)	0.459 7(2)	0.354 3(1)	0.003 96(8)	C(4b)	1.100(1)	0.203 9(7)	0.257 8(6)
S(2)	0.556 9(2)	0.143 7(1)	0.076 80(8)	C(4a)	0.028(1)	0.061 0(8)	−0.131 0(5)
O(11)	0.459 6(7)	0.306 2(5)	−0.166 0(3)	C(5b)	0.999 8(9)	0.238 3(7)	0.194 7(5)
O(12)	0.651 3(7)	0.042 2(4)	−0.066 9(3)	C(5a)	0.086 6(9)	0.112 9(7)	−0.071 0(5)
O(21)	0.067 8(7)	0.364 9(5)	−0.007 9(4)	C(11)	0.472 8(8)	0.265 4(6)	−0.118 0(4)
O(22)	0.205 1(7)	0.121 9(5)	0.122 9(3)	C(12)	0.589 6(8)	0.102 2(6)	−0.056 8(4)
O(31)	0.845 3(7)	0.476 7(5)	0.103 3(4)	C(21)	0.161 7(8)	0.316 8(6)	0.011 4(5)
O(32)	0.874 8(6)	0.222 6(5)	0.016 6(3)	C(22)	0.254 3(8)	0.164 6(6)	0.091 9(4)
O(41)	0.552 4(8)	0.042 6(5)	0.241 1(4)	C(31)	0.784 4(9)	0.408 8(6)	0.097 2(4)
O(42)	0.341 4(8)	0.669 8(5)	0.688 3(3)	C(32)	0.796 4(8)	0.248 6(6)	0.038 3(4)
O(51)	0.280 7(7)	0.566 5(5)	0.058 8(4)	C(41)	0.564(1)	0.111 8(6)	0.218 6(4)
O(52)	0.292 5(6)	0.359 3(5)	0.194 3(3)	C(42)	0.621(1)	0.291 1(6)	0.260 3(4)
O(53)	0.717 7(7)	0.503 5(5)	0.221 4(3)	C(51)	0.351 6(8)	0.503 9(6)	0.076 9(4)
N(1a)	0.221 7(6)	0.150 0(5)	−0.049 4(3)	C(52)	0.365 5(9)	0.368 4(6)	0.166 6(4)
N(1b)	0.855 7(7)	0.241 1(5)	0.177 4(3)	C(53)	0.624 3(8)	0.464 1(6)	0.179 8(4)
C(1a)	0.301 2(8)	0.138 6(6)	−0.085 5(4)				

mmol) in *m*-xylene (50 cm^3) was refluxed under nitrogen for 30 min. The solvent was removed under reduced pressure and the deep yellow residue separated by TLC [SiO_2; light petroleum (b.p. < 40 °C)–dichloromethane (4:1 v/v)] to give the cluster $[Ru_5S_2(C_5H_4N)_2(CO)_{11}]$ as ruby red crystals (0.014 g, 15%) from a dichloromethane and hexane mixture (Found: C, 24.5; H, 0.75; N, 2.75; S, 5.75. $C_{21}H_8N_2O_{11}Ru_5S_2$ requires C, 24.4; H, 0.8; N, 2.7; S, 6.2%). A minor band was discarded. Most of the material did not move from the TLC baseline even when eluting with polar solvents, which indicates considerable decomposition on heating.

X-Ray Structure Determinations for Compounds **2** *and* **4**.—Single crystals were grown by slow diffusion of methanol into a dichloromethane solution of compound **2** and by slow evaporation of a mixed dichloromethane–hexane solution of **4**. Essential details of the unit-cell parameters, data collections, structure solutions and refinements are in Table 5. The crystals were mounted on glass fibres on goniometers on the diffractometers given in Table 5, both operating with graphite-monochromated Mo-Kα radiation. Unit cells were determined by auto-indexing and least-squares fitting of 30 orientation reflections selected from rotation photographs for **2** and 23 for **4**. Intensity data were collected and corrected as given in Table 5. The structures were solved by direct methods[9] for **2** and by Patterson methods[10] for **4** and were refined by alternating cycles of full-matrix least squares and by Fourier difference syntheses.

For compound **2** all non-H atoms were refined anisotropically and H atoms were included in the final model in idealised positions riding on carbon atoms with C–H 0.96 Å and isotropic thermal parameter U = 0.08 $Å^2$. The populations of the different orientations of the C_5H_4N ligands were refined by allowing the ring atoms bonded to ruthenium to have partial populations of N and C atoms. The dominant orientation is that shown in Fig. 1 (population 0.7 ± 0.1) while the alternative minor orientation has atoms C(1a) and N(1a) replacing N(1) and C(1) in one ring and C(6a) and N(2a) replacing N(2) and C(6) in the other respectively (population 0.3 ± 0.1). Refinements with C_5H_4N ligands fixed in one or other orientation were poorer and the thermal parameters of the ruthenium-bonded atoms were less realistic.

For compound **4** all non-H atoms were refined anisotropically, H atoms were not included in the model, and the orientations of the C_5H_4N ligands as shown in Fig. 5 gave the best refinement and thermal parameters for the ruthenium-bonded atoms of the C_5H_4N rings. Anomalous dispersion effects were included in F_c and $\Delta f'$ and $\Delta f''$ and scattering factors were obtained from standard sources.[11]

All calculations were performed on MicroVax II computers using SHELXTL PLUS[9] for compound **3** and SDP/VAX[12] for **4**. Final atomic coordinates are given in Tables 6 and 7.

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

Acknowledgements

We thank the SERC and National Science Foundation for diffractometer grants, Johnson-Matthey plc for a loan of ruthenium trichloride, the SERC for a studentship (for B. R. C.), the Association of Commonwealth Universities for a studentship (for M. K.), and NATO for support for this collaboration.

References

1 A. J. Deeming and M. Karim, *Polyhedron*, 1991, **10**, 837.
2 A. J. Deeming, M. N. Meah, N. P. Randle and K. I. Hardcastle, *J. Chem. Soc., Dalton Trans.*, 1989, 2211.
3 B. R. Cockerton, A. J. Deeming, M. Karim and K. I. Hardcastle, *J. Chem. Soc., Dalton Trans.*, 1991, 431.
4 C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1975, 2092.
5 A. J. Arce, B. R. Cockerton, C. Choo Yin, A. J. Deeming, M. B. Hursthouse, L. New and N. P. C. Walker, unpublished work.
6 G. Conole, M. McPartlin, H. R. Powell, T. Dutton, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1989, 379, C1.
7 V. A. Maksakov, V. A. Ershova, V. P. Kirin, I. F. Golavaneva, A. Ya. Mikhailova and A. P. Klyagina, *Dokl. Akad. Nauk SSSR*, 1988, **299**, 116.
8 M. R. Churchill, F. J. Hollander and J. P. Hutchinson, *Inorg. Chem.*, 1977, **16**, 2655.
9 G. M. Sheldrick, SHELXTL-PLUS, An integrated system for refining and displaying crystal structures from diffraction data, University of Göttingen, 1986.
10 G. M. Sheldrick, SHELXS 86, Program for crystal structure solution, University of Göttingen, 1986.
11 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.
12 B. A. Frenz, in *Computing in Crystallography*, eds. H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld and G. C. Bassi, Delft University, 1978, pp. 64–71.

Received 15*th November* 1991; *Paper* 1/05803G