# Unusual Properties of Metal Complexes involving Acyclic Polydentate Thioether Ligands. Copper, Nickel and Palladium Complexes of 3,6,9,12,15-Pentathiaheptadecane†

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The ligand 3,6,9,12,15-pentathiaheptadecane and its complexes $[CuL][X]_2$ ($X = ClO_4^-$ or $CF_3SO_3^-$), $[Cu_2Cl_3L]$ (a mixed-valence compound), $[NiL(H_2O)][Y]_2$ ($Y = ClO_4^-$ or $BF_4^-$) and $[PdL][ClO_4]_2$ were prepared and X-ray crystal structure determinations of $[CuL][ClO_4]_2$ and $[NiL(H_2O)][ClO_4]_2$ were carried out. The compounds have been examined by cyclic voltammetry, magnetic susceptibility, electronic spectroscopy and ESR or variable-temperature NMR spectroscopy. The $[CuL][X]_2$ salts have the highest value of $E_{\frac{1}{2}}$ for the $Cu^{II}$–thioether systems reported so far and an assessment of the reasons for the high redox potential suggests it to be related to both destabilization of the $Cu^{II}$ state and more importantly to stabilization of the $Cu^I$ state by the ligand. The absence of ring strain in the complexed acyclic ligand and entropy effects are considered to be significant contributors. There is evidence that the nickel co-ordination sphere remains intact in solutions of $[NiL(H_2O)][Y]_2$ and relationships between structural and spectral parameters such as $\Delta_0$ and the nephelauxetic ratio, $\beta$, have been investigated. Although $\Delta_0$ is mainly sensitive to donor type, $\beta$ is found to be very sensitive to bond length. A variable-temperature NMR study of $[PdL][ClO_4]_2$ is treated as evidence for an unprecedented fluxional activity involving movement of a thioether donor from the 'top' to the 'bottom' of a co-ordination plane while inversion at five thioether donors is also occurring.

The properties of thioether–transition metal complexes are of continuing interest as is adjustment of their properties by appropriate combinations of ligand and metal.[1,2] Simple complexes of copper have been studied in particular because of their similarity to systems found in Nature[3] and, as part of these studies, attempts have been made to model both thermodynamic and kinetic features of the natural redox systems and processes based on copper.[4,5] More recently, interest has developed in thioether complexes of nickel[6,7] because of the discovery that a number of hydrogenases contain nickel with several sulfurs in the co-ordination sphere at the enzyme active site.[8] Complexes of Group 6 and Group 8 transition metals with thioethers have been examined extensively[9,10] because of their stereochemically non-rigid properties and interest continues in the consequences and applications of these metal complexes.[11–13]

Owing to the comparatively poor co-ordinating ability of monodentate thioethers relative to amines or phosphines, it has become common practice in all these studies to use macrocyclic thioethers to stabilize complexes even though the macrocyclic effect is often smaller for thioethers than for their ethereal counterparts.[14] As a result of this practice, it is of interest to compare the properties of complexes derived from acyclic polythioethers, in which conformational and other structural restrictions associated with cyclic ligands do not occur, with those derived from medium-sized cyclic or macrocyclic analogues. Our general interest in steric and structural effects in thioethers and their complexes[15,16] has led us to prepare the acyclic $S_5$ donor $EtSCH_2(CH_2SCH_2)_3CH_2SEt$ (L) and several of its metal complexes.

## Results and Discussion

Treatment of bis(2-mercaptoethyl) sulfide with 2-chloroethyl ethyl sulfide in basic medium gives, after recrystallization, >80% yield of the crystalline ligand L. Although the mass spectrum of white crystals of L showed only major fragment peaks and not a parent-ion peak, NMR data and the crystal structure of $[CuL][ClO_4]_2$ confirm its synthesis.

Addition of a dichloromethane solution of the ligand to an acetonitrile solution of $Cu(ClO_4)_2$ or $Cu(CF_3SO_3)_2$ results in immediate precipitation in >80% yield of the reddish brown five-co-ordinate cation $[CuL]^{2+}$ as the appropriate salt. Suitable crystals for X-ray structure diffraction studies can be grown by vapour diffusion of diethyl ether into a solution of the complex in nitromethane. The results of a study on the $ClO_4^-$ salt are shown in Tables 1 and 2 and Fig. 1.

The co-ordination sphere about copper is a slightly distorted square-based pyramid in which the distortion is caused by the terminal thioether sulfurs drooping ≈20° below the base plane of the pyramid. The copper atom and the apical sulfur lie in a plane of symmetry which relates the two ends of the ligand chain. In the unit cell there are two independent cations each lying on the plane of symmetry so that in one Cu(1) and S(3) are in the plane and in the other Cu(2) and S(6) are in the plane. The mean bond distances within the co-ordination spheres are 2.351(5), 2.356(5) and 2.502(7) Å. The two shorter distances are from copper to basal thioether sites while the longest is to the apical site. As usual, the apical bond is longer than the basal bonds,[16] in this case by 0.13 Å. All are 'normal' bond lengths[16] but show slight lengthening and greater uniformity compared to those in the analogous five-co-ordinate macrocyclic complex $[Cu([15]aneS_5)][ClO_4]_2$ ($[15]aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane), which are 2.289(2), 2.315(2), 2.331(2), 2.338(2) (basal) and 2.398(2) (apical) Å.[17] These effects most likely reflect the somewhat greater freedom of the acyclic ligand compared to its cyclic analogue. Finally, there are four independent perchlorate ions, all with their chlorine atoms in the plane of symmetry, and three of the anions are disordered.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

*Non-SI units employed:* $G = 10^{-4} T$, $\mu_B \approx 9.274\,02 \times 10^{-24}\ J\ T^{-1}$.

**Table 1** Atomic coordinates for $[CuL][ClO_4]_2$

| Atom | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|
| Cu(1) | 0.7739(2) | 0.25 | 0.1639(1) | 0.5 |
| Cu(2) | 0.2836(2) | 0.25 | 0.4104(1) | 0.5 |
| Cl(1) | 0.3710(5) | 0.25 | 0.6313(2) | 0.5 |
| Cl(2) | 0.2588(5) | 0.25 | 0.0239(3) | 0.5 |
| Cl(3) | 0.7843(6) | 0.25 | 0.3724(3) | 0.5 |
| Cl(4) | 0.8445(6) | 0.25 | 0.7976(4) | 0.5 |
| S(1) | 0.6392(4) | 0.0958(5) | 0.1852(2) | 1.0 |
| S(2) | 0.9194(3) | 0.0924(5) | 0.1828(2) | 1.0 |
| S(3) | 0.7841(6) | 0.25 | 0.0332(3) | 0.5 |
| S(4) | 0.1703(3) | 0.0955(4) | 0.4524(2) | 1.0 |
| S(5) | 0.4227(3) | 0.0923(5) | 0.4038(2) | 1.0 |
| S(6) | 0.2307(5) | 0.25 | 0.2741(3) | 0.5 |
| O(1) | 0.4021 | 0.2893 | 0.5647 | 0.5 |
| O(2) | 0.4546 | 0.2988 | 0.6919 | 0.5 |
| O(3) | 0.3741 | 0.1126 | 0.6347 | 0.5 |
| O(4) | 0.2561 | 0.2925 | 0.6342 | 0.5 |
| O(5) | 0.3039 | 0.1953 | 0.0946 | 0.5 |
| O(6) | 0.3302 | 0.2051 | −0.0257 | 0.5 |
| O(7) | 0.2604 | 0.3823 | 0.0274 | 0.5 |
| O(8) | 0.1404 | 0.2039 | −0.0017 | 0.5 |
| O(9) | 0.718(1) | 0.146(2) | 0.3680(7) | 1.0 |
| O(10) | 0.869(1) | 0.25 | 0.4382(8) | 0.5 |
| O(11) | 0.838(1) | 0.25 | 0.3121(8) | 0.5 |
| O(12A) | 0.9438 | 0.2381 | 0.8610 | 0.3 |
| O(12B) | 0.7341 | 0.2484 | 0.7455 | 0.2 |
| O(13A) | 0.8238 | 0.3724 | 0.7782 | 0.3 |
| O(13B) | 0.8815 | 0.3676 | 0.8197 | 0.2 |
| O(14A) | 0.7447 | 0.1895 | 0.8200 | 0.3 |
| O(14B) | 0.9318 | 0.1931 | 0.7554 | 0.2 |
| O(15A) | 0.8753 | 0.1726 | 0.7405 | 0.3 |
| O(15B) | 0.8404 | 0.1622 | 0.8542 | 1.0 |
| C(1) | 0.478(2) | −0.070(2) | 0.110(1) | 1.0 |
| C(2) | 0.560(1) | 0.037(2) | 0.100(1) | 1.0 |
| C(3) | 0.738(2) | −0.034(2) | 0.2202(9) | 1.0 |
| C(4) | 0.834(2) | −0.052(2) | 0.1781(9) | 1.0 |
| C(5) | 0.969(2) | 0.088(2) | 0.099(1) | 1.0 |
| C(6) | 0.876(2) | 0.119(2) | 0.030(1) | 1.0 |
| C(7) | −0.005(2) | −0.070(2) | 0.389(1) | 1.0 |
| C(8) | 0.072(1) | 0.041(2) | 0.3724(8) | 1.0 |
| C(9) | 0.272(1) | −0.031(2) | 0.4711(8) | 1.0 |
| C(10) | 0.346(1) | −0.050(2) | 0.4129(9) | 1.0 |
| C(11) | 0.428(1) | 0.090(2) | 0.3086(8) | 1.0 |
| C(12) | 0.314(1) | 0.116(2) | 0.2548(8) | 1.0 |

**Table 2** Selected bond lengths (Å) and angles (°) for $[CuL][ClO_4]_2$

| | | | |
|---|---|---|---|
| Cu(1)–S(1) | 2.359(5) | Cu(2)–S(4) | 2.343(5) |
| Cu(1)–S(2) | 2.358(5) | Cu(2)–S(5) | 2.353(5) |
| Cu(1)–S(3) | 2.489(7) | Cu(2)–S(6) | 2.515(6) |
| S(1)–Cu(1)–S(1′) | 87.7(3) | S(4)–Cu(2)–S(4′) | 88.7(2) |
| S(1)–Cu(1)–S(2) | 88.2(2) | S(4)–Cu(2)–S(5) | 88.0(2) |
| S(1)–Cu(1)–S(2′) | 161.9(2) | S(4)–Cu(2)–S(5′) | 163.5(2) |
| S(1)–Cu(1)–S(3) | 109.7(2) | S(4)–Cu(2)–S(6) | 107.9(2) |
| S(2)–Cu(1)–S(2′) | 90.2(2) | S(5)–Cu(2)–S(5′) | 90.6(2) |
| S(2)–Cu(1)–S(3) | 88.3(2) | S(5)–Cu(2)–S(6) | 88.5(2) |

Primed atoms are related to unprimed ones by the relation $x, \frac{1}{2} - y, z$.

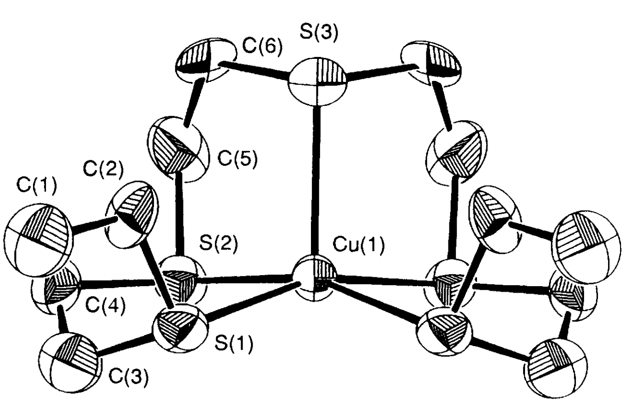

**Fig. 1** The complex cation $[CuL]^{2+}$

The ESR spectra of the $[CuL]^{2+}$ cation in both the solid state and in solution are consistent with its X-ray crystal structure. Powder spectra at room temperature have two *g* values. For the $ClO_4^-$ salt, $g_{\parallel} = 2.109$ and $g_{\perp} = 2.030$. In $CH_3NO_3$ solution at room temperature the spectrum consists of four lines with $g_0 = 2.057$ and $A_0 = 72 \times 10^{-4}$ cm$^{-1}$. As a 'glass' in the same solvent at 77 K, $g_{\parallel} = 2.091$, $g_{\perp} = 2.025$ and $A_{\parallel} = 161 \times 10^{-4}$ cm$^{-1}$. Data for the $CF_3SO_3^-$ salt are similar. For the powder, $g_{\parallel} = 2.109$ and $g_{\perp} = 2.031$. In $CH_3NO_3$ solution at room temperature the spectrum consists of four lines with $g_0 = 2.060$ and $A_0 = 82 \times 10^{-4}$ cm$^{-1}$. As a 'glass' in the same solvent at 77 K, $g_{\parallel} = 2.090$, $g_{\perp} = 2.018$ and $A_{\parallel} = 156 \times 10^{-4}$ cm$^{-1}$.

Infrared spectra of the $ClO_4^-$ salt as a Nujol mull show a broad strong band at 1096 cm$^{-1}$ indicative of unco-ordinated $ClO_4^-$ as confirmed by the X-ray study. The $CF_3SO_3^-$ salt under similar conditions exhibits strong infrared bands at 1266, 1092 and 622 cm$^{-1}$ which are consistent with unco-ordinated triflate. Thus, in the solid state, both anions appear to be unco-ordinated. In solution, there is no direct evidence from this study to indicate whether anions or solvent are co-ordinated in the sixth co-ordination site below the base of the square-pyramidal co-ordination sphere. It seems likely, however, that either an anion or a solvent molecule occupies this site as has been observed for other related systems.[16,18]

The electronic spectra of the two salts are similar in both the solid state and in solution. For example, in acetonitrile the spectrum of the $ClO_4^-$ salt consists of four main bands at $\lambda_{max} = 880$ (210), 556 (1480), 435 (8800) and 255 nm (2420 dm$^3$ mol$^{-1}$ cm$^{-1}$) in addition to a shoulder at 350 nm on the high-energy side of the 435 nm band. The high-energy bands at 350 and 435 nm are, by analogy to other systems, assigned to equatorial S $\longrightarrow$ Cu charge-transfer transitions while that at 255 nm is due to an apical S $\longrightarrow$ Cu charge transfer.[19–21] The lower energy bands at 880 and 556 nm are d–d transitions the intensities of which are enhanced by the less-than-perfect octahedral symmetry and by intensity borrowing from the nearby charge-transfer band.[20] The presence of two well separated d–d bands in the solution spectrum is consistent with a distorted square-pyramidal co-ordination sphere with considerable axial interaction[20] suggesting that the structure of the metal–ligand system observed in the solid state is maintained in solution with, of course, the probability of additional interaction in the open or sixth co-ordination site on copper by the anion or a solvent molecule.[16,18]

Cyclic voltammograms of $[CuL]^{2+}$ as either salt in acetonitrile are identical which suggests that the co-ordination spheres are similar. This could be due to solvation in the open co-ordination site or more likely it is due to the presence of an oxygen donor from the anion that occupies the sixth co-ordination site in solution as has been observed for other five-co-ordinate copper complexes.[16,18,22] The ratio $i_{pc}/i_{pa} = 1$ ($i_{pc}$ is the cathodic peak current and $i_{pa}$ is the corresponding anodic peak current) and the peak separation, $\Delta E_p$, is 78 mV at all scan rates between 50 and 300 mV s$^{-1}$. These observations indicate a reversible redox process. Since solutions of the ligand under similar conditions show no electrochemical activity in the same voltage range, the waves are attributed to redox activity at the complexed metal atom.

It is noteworthy that this cation with $E_{\frac{1}{2}} = 1.08$ V *vs.* the

**Table 3** Atomic coordinates for $[NiL(H_2O)][ClO_4]_2$

| Atom | *x* | *y* | *z* | Occupancy |
|---|---|---|---|---|
| Ni | 0.217 53(7) | 0.335 51(4) | 0.218 72(6) | 1.0 |
| Cl(1) | 0.773 8(2) | 0.175 62(9) | 0.060 3(1) | 1.0 |
| Cl(2) | 0.291 0(2) | 0.053 58(9) | 0.225 8(1) | 1.0 |
| S(1) | 0.085 0(2) | 0.398 54(9) | 0.077 8(1) | 1.0 |
| S(2) | 0.034 9(2) | 0.338 81(9) | 0.322 7(1) | 1.0 |
| S(3) | 0.286 5(2) | 0.448 84(9) | 0.296 3(1) | 1.0 |
| S(4) | 0.355 9(2) | 0.277 6(1) | 0.359 0(1) | 1.0 |
| S(5) | 0.398 4(2) | 0.319 60(8) | 0.113 1(1) | 1.0 |
| O(1) | 0.153 2(4) | 0.231 3(2) | 0.161 0(3) | 1.0 |
| O(2) | 0.909 8(4) | 0.168 5(3) | 0.095 5(4) | 1.0 |
| O(3) | 0.753 7(9) | 0.247 3(5) | 0.017 5(7) | 0.7 |
| O(3A) | 0.721(2) | 0.244 1(9) | 0.052(1) | 0.3 |
| O(4) | 0.735 3(8) | 0.123 5(4) | −0.014 6(7) | 0.7 |
| O(4A) | 0.761(2) | 0.141 2(9) | −0.051(1) | 0.3 |
| O(5) | 0.702(1) | 0.165 4(6) | 0.151 4(9) | 0.7 |
| O(5A) | 0.690(2) | 0.136(1) | 0.120(2) | 0.3 |
| O(6) | 0.183 5(8) | 0.040 2(4) | 0.157 5(7) | 1.0 |
| O(7) | 0.335(1) | 0.124 6(6) | 0.224 3(8) | 0.55 |
| O(7A) | 0.413(2) | 0.076(1) | 0.181(1) | 0.45 |
| O(8) | 0.279(1) | 0.024 3(9) | 0.324(1) | 0.55 |
| O(8A) | 0.258(1) | 0.113 1(7) | 0.288(1) | 0.45 |
| O(9) | 0.374(2) | 0.014(1) | 0.177(2) | 0.55 |
| O(9A) | 0.340(1) | −0.003 7(5) | 0.291 5(8) | 0.45 |
| C(1) | −0.057 4(8) | 0.368 5(4) | −0.117 9(6) | 1.0 |
| C(2) | 0.030 2(7) | 0.334 8(4) | −0.026 8(5) | 1.0 |
| C(3) | −0.062 2(7) | 0.417 2(4) | 0.139 5(6) | 1.0 |
| C(4) | −0.098 6(6) | 0.362 4(4) | 0.221 8(6) | 1.0 |
| C(5) | 0.059 6(7) | 0.418 8(4) | 0.403 3(5) | 1.0 |
| C(6) | 0.142 4(7) | 0.477 3(4) | 0.357 3(6) | 1.0 |
| C(7) | 0.402 7(7) | 0.424 1(4) | 0.409 4(6) | 1.0 |
| C(8) | 0.384 4(7) | 0.349 4(4) | 0.454 3(5) | 1.0 |
| C(9) | 0.510 4(6) | 0.266 7(4) | 0.302 5(5) | 1.0 |
| C(10) | 0.536 4(6) | 0.318 0(4) | 0.216 2(6) | 1.0 |
| C(11) | 0.432 3(7) | 0.401 0(4) | 0.044 4(6) | 1.0 |
| C(12) | 0.554 9(7) | 0.398 1(4) | −0.011 0(6) | 1.0 |

**Table 4** Selected bond lengths (Å) and angles (°) in $[NiL(H_2O)][ClO_4]_2$

| | | | |
|---|---|---|---|
| Ni–S(1) | 2.425(2) | Ni–S(2) | 2.388(2) |
| Ni–S(3) | 2.404(2) | Ni–S(4) | 2.404(2) |
| Ni–S(5) | 2.403(2) | Ni–O(1) | 2.153(4) |
| S(1)–Ni–S(2) | 88.79(7) | S(1)–Ni–S(3) | 89.45(6) |
| S(1)–Ni–S(4) | 177.37(7) | S(1)–Ni–S(5) | 93.38(6) |
| S(1)–Ni–O(1) | 93.5(1) | S(2)–Ni–S(3) | 88.16(6) |
| S(2)–Ni–S(4) | 92.47(7) | S(2)–Ni–S(5) | 174.35(6) |
| S(2)–Ni–O(1) | 88.8(1) | S(3)–Ni–S(4) | 88.29(6) |
| S(3)–Ni–S(5) | 97.07(6) | S(3)–Ni–O(1) | 175.7(1) |
| S(4)–Ni–S(5) | 85.58(6) | S(4)–Ni–O(1) | 88.8(1) |
| S(5)–Ni–O(1) | 85.9(1) | | |

normal hydrogen electrode (NHE) has the highest redox potential for a $Cu^{II}$–$Cu^I$ couple with exclusively thioether donors yet reported. For comparison, the five-co-ordinate copper(II) complex with [15]ane$S_5$ has a $E_{\frac{1}{2}}$ value roughly 400 mV less than that of $[CuL]^{2+}$.[23]

The high potential exhibited by our system must be due either to exceptional stabilisation of copper(I) or to exceptional destabilisation of copper(II) or perhaps to a combination of both effects. It has been observed repeatedly that substituting thioether for amine donors in the co-ordination sphere of copper(II) results in a predictable increase in the $Cu^{II}$–$Cu^I$ potential.[1,2,16,24] As a result of studies of the stability constants of several related complexes of both $Cu^{II}$ and $Cu^I$, the view has been expressed that dependence of the $Cu^{II}$–$Cu^I$ potential on the relative number of N- and S-donor atoms is almost entirely due to destabilization of $Cu^{II}$ with an increasing ratio of S to N donors rather than to increased stabilization of $Cu^I$.[1] This view is in contrast to popular beliefs concerning enhanced stabilization of $Cu^I$ by 'soft' donors such as thioether sulfur and was based on the evidence that there is little difference in the stability of comparable N- and S-donor complexes of $Cu^I$.

To assess the source of the increased potential exhibited by our system, it is useful to compare the behaviour of other related systems. Stability constants for the $Cu^{II}$ complexes of the tetradentate homoleptic thioether donors [14]ane$S_4$ (1,4,8,11-tetrathiacyclotetradecane), a cyclic ligand, and its open-chain analogue $EtS(CH_2)_2S(CH_2)_3S(CH_2)_2SEt$ have been determined[22] and show that upon going from a cyclic to an open-chain ligand there is destabilization of $Cu^{II}$ complexes ($K = 2.18 \times 10^4$ and $K = 1.51 \times 10^2$ respectively) which can be attributed to the greater loss of entropy by the acyclic ligand upon complex formation. Assuming a similar destabilization for the acyclic analogue of [15]ane$S_5$ we could expect the $Cu^{II}$ complex of L to be at least two orders of magnitude less stable than the cyclic ligand which has a stability constant $K = 1.53 \times 10^4$ under similar conditions.[1]

Stability constants for the $Cu^I$ complexes of [14]ane$S_4$ ($K = 1 \times 10^{12}$ dm$^3$ mol$^{-1}$)[1] and $EtS(CH_2)_2S(CH_2)_3S(CH_2)_2SEt$ ($K = 2 \times 10^{17}$ dm$^3$ mol$^{-1}$)[25] show that there is stabilization of $Cu^I$ upon changing from a cyclic to an acyclic ligand. This can be attributed partly to the change from an $S_3O$ *solution* donor set in the [14]ane$S_4$ species to an $S_4$ donor set in the $EtS(CH_2)_2S(CH_2)_3S(CH_2)_2SEt$ species but primarily to the differences in strain in the complexed ligands.[14,25] This interpretation is supported by comparison of the stability constants of the $Cu^I$ complexes of $EtS(CH_2)_2S(CH_2)_3S(CH_2)_2SEt$ ($K = 2 \times 10^{17}$ dm$^3$ mol$^{-1}$)[25] and [15]ane$S_5$ ($K = 4 \times 10^{13}$ dm$^3$ mol$^{-1}$).[1] Both complexes have four sulfurs bound to $Cu^I$ and even though there is an unfavourable entropy change for complexation of the acyclic ligand relative to the cyclic one, the complex formed by the acyclic ligand is still four orders of magnitude more stable. Assuming similar stabilization when the cyclic ligand [15]ane$S_5$ and its acyclic analogue L are compared, we could expect the $Cu^I$ complex of L to be about four orders of magnitude more stable than that of [15]ane$S_5$ for which $K = 4 \times 10^{13}$ dm$^3$ mol$^{-1}$ under similar conditions.

Using the appropriate form of the Nernst equation (1) with

$$E_f = E^{0\prime}{}_{aq} - \frac{2.303RT}{nF} \log \frac{K_{[Cu^{II}L]}}{K_{[Cu^{I}L]}} \quad (1)$$

$E^{0\prime}{}_{aq} = 0.13$,[1] $K_{[Cu^{II}L]} = 1.5 \times 10^2$ dm$^3$ mol$^{-1}$ and $K_{[Cu^IL]} = 4 \times 10^{17}$ dm$^3$ mol$^{-1}$ as discussed above, a value of $E_f = 1.04$ V *versus* NHE in water can be estimated for the Cu–L system. By using Addison's criteria for conversion of experimental data in acetonitrile into predicted values in aqueous medium,[2] namely, $E_{aq} = 0.96\ E_{acetonitrile} - 0.004$, a value of 1.03 V *vs.* NHE for our complex is obtained in water which compares favourably with the value of 1.04 V estimated above. On the basis of this analysis, the enhanced potential displayed by our complex is due in part to destabilization of $Cu^{II}$ but more importantly to stabilization of $Cu^I$ resulting mainly from entropy effects and the absence of macrocycle ring strain.

When $CuCl_2$ is treated with the ligand L, the resulting reddish brown solid appears by analysis to be a mixed-valence species of empirical formula $[Cu_2Cl_3L]$. The ESR spectrum of a powdered sample of the solid at room temperature shows a featureless signal centred at $g = 2.086$ having a peak-to-peak width of about 250 G. This would be consistent with the presence of grossly misaligned tetragonal copper(II) sites in the unit cell but conveys no real structural information. The electronic spectrum of the material as a Nujol mull shows a single broad band centred at 475 nm with a shoulder at 625 nm. These features are more clearly discernible in acetonitrile where the spectrum consists of an absorption at 700 nm ($\varepsilon$ = 500 dm$^3$ mol$^{-1}$ cm$^{-1}$) with a long-wavelength tail assignable to a d–d transition and bands assignable to charge-transfer transitions at 420 (sh), 340 ($\varepsilon$ = 6400) and 250 nm ($\varepsilon$ = 4700 dm$^3$ mol$^{-1}$ cm$^{-1}$). Such spectra are consistent with pseudo-octahedral or square-pyramidal co-ordination geometry about copper(II) involving sulfur and chlorine donors and are very similar to spectra we have reported previously.[18,21] Cyclic voltammetry in acetonitrile shows two overlapping quasi-reversible waves. One has $E_{\frac{1}{2}}$ = 724 mV *vs.* NHE and $\Delta E_p$ = 190 mV at all scan speeds between 50 and 500 mV s$^{-1}$ and is similar to the wave exhibited by related systems with thioether and chlorine bound to Cu$^{II}$.[16,18] The other has $E_{\frac{1}{2}}$ = 795 mV *vs.* NHE and $\Delta E_p$ = 330 mV at all scan speeds between 50 and 500 mV s$^{-1}$. The electrochemical evidence indicates that there are two different copper sites in the compound. One behaves similarly to sites in $Cu^{II}Cl_xS_y$ species that we have studied previously in both the solid and solution states[16,18] but the other site behaves somewhat differently. The former site appears electrochemically and spectroscopically to have both chlorine and thioether bound to Cu$^{II}$ in both the solid and in solution. The second site is therefore the Cu$^{I}$ site in the brown solid and would be expected to have a different co-ordination geometry thereby giving it different electrochemical characteristics than those of the Cu$^{II}$ site. The nature of the co-ordination geometry at this second site is not clear since the electrochemical response is not like that of a known system[26] and the spectroscopic signature of the Cu$^{I}$ is obscured by the presence of Cu$^{II}$ and its donors. Our attempts to grow crystals of this substance suitable for X-ray examination have so far been unsuccessful.

Preparation of the nickel complexes $[NiL(H_2O)][ClO_4]_2$ and $[NiL(H_2O)][BF_4]_2$ is unremarkable. Both the $ClO_4^-$ and $BF_4^-$ salts have a molecule of water per formula unit which is probably co-ordinated to the metal in both cases as in the crystal structure of the $ClO_4^-$ salt (Fig. 2 and Tables 3 and 4). The complex cation $[NiL(H_2O)]^{2+}$ has a nearly perfectly octahedral co-ordination sphere about nickel and its perchlorate anions are each disordered in two orientations about one Cl–O bond.

The greatest deviation in bond angles is at S(2)–Ni–S(5) which is 5.65° less than the ideal angle of 180°. Bond distances are typical for octahedral nickel with an apical Ni–S(3) bond of 2.404(2) Å and basal distances of 2.425(2), 2.388(2), 2.404(2) and 2.403(2) Å. These values compare favourably with those in the centrosymmetric complex $[Ni([18]aneS_6)]^{2+}$ ($[18]aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane) of 2.389(1), 2.397(1) and 2.377(1) Å[27] but are longer at the basal sites than those in $[Ni([15]aneS_5)]^{2+}$ of 2.413(5) (apical) and 2.146(7), 2.169(6), 2.177(6) and 2.198(6) Å (basal)[28] where some strain exists as the ring conforms to the necessary geometry about the nickel atom. The Ni–O distance to the co-ordinated water molecule of 2.153(4) Å is slightly longer than corresponding distances to the two water molecules in the centrosymmetric complex $[Ni([16]aneS_4)(H_2O)_2]^{2+}$ ($[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane) of 2.083(3) Å.[28] The magnetic moment ($\mu_{eff}$) of the $ClO_4^-$ complex at 22 °C is 2.95 $\mu_B$ as expected for a pseudo-octahedral species with two unpaired electrons. Electronic spectra of the salts as solids or as solutions in acetonitrile or nitromethane are typical of six-co-ordinate nickel(II) and have bands at 318 ($\varepsilon$ = 2700) (charge transfer), 535 (20) (d–d) and 860 nm (50 dm$^3$ mol$^{-1}$ cm$^{-1}$) (d–d) with a shoulder at 1075 nm which show no significant dependence upon state or solvent. This suggests the co-ordination sphere remains intact as the complex passes into solution, at least in these two solvents. The third d–d band expected for a complex of Ni$^{II}$ with this co-ordination geometry is obscured by the charge-transfer band. By using the two observed d–d bands ($\nu_1$ and $\nu_2$) and equation

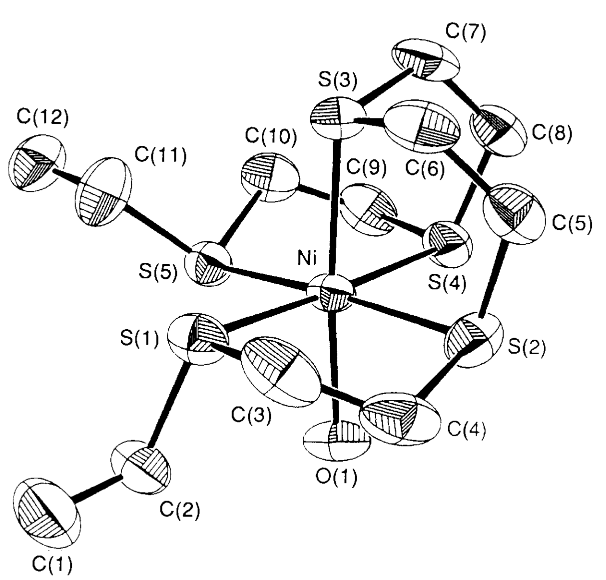

**Fig. 2** The complex cation $[NiL(H_2O)]^{2+}$

(2) a value for $B$, the Racah parameter, of 964 cm$^{-1}$ is obtained,

$$B = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1) \qquad (2)$$

which gives a value of 0.93 for the nephelauxetic ratio $\beta$ (= $B_{complex}/B_{free\ ion}$) when $B_{free\ ion}$ = 1038 cm$^{-1}$.[29] The lowest energy band gives the value of $\Delta_0$ = 11 696 cm$^{-1}$. The ligand-field strength experienced by Ni in this complex is comparable to that in bis(2,5,8-triathianonane)nickel(II) (11 800 cm$^{-1}$ [27]) but the nephelauxetic effect in the present case is less at 0.93 than that obtained with two 2,5,8-trithianonane ligands (0.70).[27] These observations, when considered with crystal structural results reveal a considerable sensitivity of ligand-field parameters to small structural changes. For example, $[Ni([15]aneS_5)(CH_3CN)]^{2+}$ has four Ni–S bonds that are approximately 0.25 Å shorter than those in $[NiL(H_2O)]^{2+}$ (Table 4) and has a roughly comparable value for $\Delta_0$ (11 090 cm$^{-1}$) but a significantly greater nephelauxetic effect ($\beta$ = 0.78).[28] Likewise, $[Ni([18]aneS_6)]^{2+}$ has only slightly shorter bond lengths to all six sulfurs than those in $[NiL(H_2O)]^{2+}$ and its values for $\Delta_0$ (12 290 cm$^{-1}$) and $\beta$ (0.83) show the same trend.[27]

The electronic spectrum of the purple complex $[PdL][ClO_4]_2$ consists of bands at 500 ($\varepsilon$ = 200) and 290 nm (23 220 dm$^3$ mol$^{-1}$ cm$^{-1}$) which show little solvent dependence but are shifted slightly in solution from their positions in the solid state of 540 and 325 nm. This spectrum is consistent with a five-co-ordinate square-pyramidal Pd$^{II}$ cation.[30-32] Such a structure would also be consistent with the NMR spectrum and would be comparable to that of the copper complex described earlier. NMR signals of all the $CH_2CH_2$ hydrogens in the palladium complex are shifted 0.3 to 0.9 ppm to lower field from their positions in the free ligand. This is analogous to behaviour observed for signals from methylene groups adjacent to co-ordinated thioether sulfurs in related complexes but unlike that of $CH_2$ groups adjacent to free thioethers which are shifted very little by co-ordination of remote donors.[11,13,32] Therefore, it seems likely that all sulfurs are co-ordinated although the apical sulfur is probably only weakly bound.[31] Were one thioether to remain completely free, a signal would be expected from its adjacent methylenes at higher field than is observed.

The NMR spectra of $[PdL][ClO_4]_2$ show temperature dependence (Fig. 3) suggesting that inversions at co-ordinated sulfurs are occurring. This behaviour is similar to that reported by several authors for palladium- and platinum-chelated

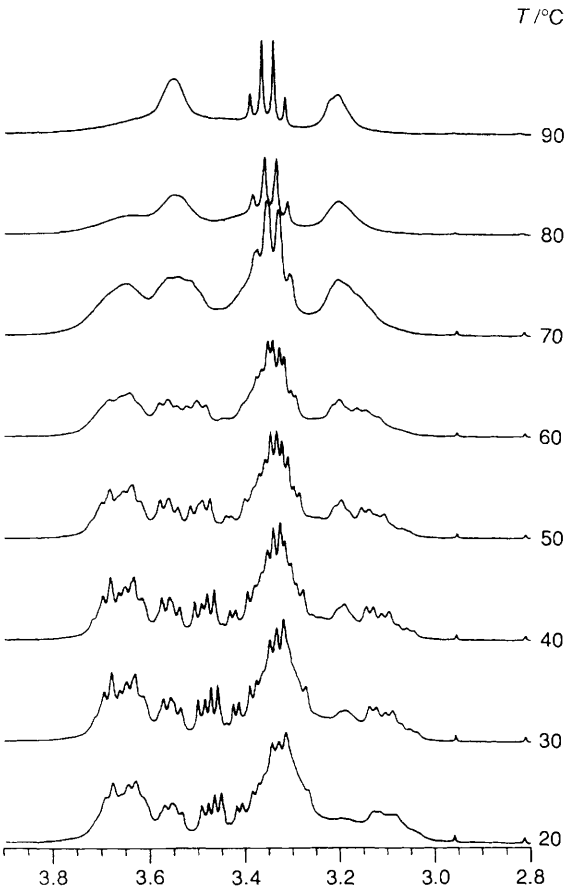

**Fig. 3** Variable-temperature $^1H$ NMR spectra of $[PdL][ClO_4]_2$ in $CD_3NO_2$

thioethers in acyclic and macrocyclic ligands.[9,11-13] Thus in Fig. 3 the spectrum obtained at 90 °C exhibits a quartet at about δ 3.35 due to the $CH_2$ hydrogens of the ethyl groups. A single quartet is observed because the sulfurs to which the ethyls are attached are undergoing rapid inversions and the $CH_2$ environment is averaged on the NMR time-scale. As the sample is cooled, the rates of inversion at the sulfur atoms slow down and the signal eventually splits at low temperatures into overlapping AB quartets due to three isomers, one with both ethyl groups 'up' with respect to the basal plane, one with both 'down' and one with an 'up' and a 'down' arrangement. Similar inversions are occurring at all the other sulfurs as well since all portions of the spectrum simplify with rising temperature. As is apparent from molecular models, the complex cation is rigid over the central three sulfurs of the ligand chain and inversions at the two basal thioethers remote from the ethyl groups cannot occur if the apical thioether remains bound to the metal. Furthermore, if it dissociates and the two basal thioethers then invert, the apical thioether cannot return to its original location but must instead return to the corresponding site on the opposite side of the basal plane. This requires substantial atomic movement and as a result, a high temperature limiting spectrum is not obtained even at 90 °C, the highest temperature achieved with non-reactive solvents. We believe this cation represents not only the first example of this type of fluxional behaviour but also the most extreme example of multiple-site inversions known at present.

## Experimental

*General.*—Commercially available reagents were obtained from Aldrich or Morton Thiokol Alfa Products and were used without further purification. Those used for cyclic voltammetry measurements were of spectroscopic grade. Spectroscopic data were obtained using the following instruments: IR, Mattson Polaris (FT) Fourier-transform spectrometer; UV/VIS, Cary model 5E spectrometer; ESR, Bruker ESP-300 X-band spectrometer operating at ≈9.5 GHz. Magnetic susceptibility data were obtained at room temperature by the Faraday method. Electrochemical measurements were carried out under a nitrogen atmosphere at room temperature using a BAS CV27 voltammograph and a Houston 2000 Omnigraph X-Y recorder. Solution concentrations were $10^{-3}$ mol $dm^{-3}$ in complex and 0.1 mol $dm^{-3}$ in supporting electrolyte (tetraethylammonium perchlorate). Voltammograms were recorded using a glassy carbon working electrode that was pre-polished with 0.3 µm $Al_2O_3$, a platinum counter electrode and an aqueous saturated calomel reference electrode checked periodically relative to a $1.0 \times 10^{-3}$ mol $dm^{-3}$ solution of ferrocene in dimethyl sulfoxide containing 0.1 mol $dm^{-3}$ tetraethylammonium perchlorate for which the ferrocene–ferrocenium reduction potential was 400 mV and $\Delta E_p$ was 72 mV at a scan rate of 100 mV $s^{-1}$. The reference electrode was separated from the bulk of the solution by a porous Vycor tube. Junction potential corrections were not used and potentials reported *versus* the NHE were obtained by adding 0.244 V to values obtained *versus* the saturated calomel electrode. Analyses were performed by Canadian Microanalytical Service Ltd.

*Preparations.*—3,6,9,12,15-Pentathiaheptadecane, L. Sodium metal (2.3 g, 0.10 mol) was dissolved in commercial absolute ethanol (200 $cm^3$) under an atmosphere of dry nitrogen and bis(2-mercaptoethyl) sulfide (7.7 g, 0.050 mol) was added cautiously. The resulting mixture was heated to reflux and to it was added a solution of 2-chloroethyl ethyl sulfide (12.5 g, 0.100 mol) dropwise with stirring over a period of 2 h. Refluxing and stirring were continued for a further 1 h when volatiles were removed on a rotary evaporator and the residue extracted with $CHCl_3$ (3 × 50 $cm^3$). The extracts were washed with water several times, dried over anhydrous $CaCl_2$ and taken to dryness to give the crude product which was recrystallized from chloroform–methanol (50:50) to yield 13.5 g (82%) of white crystals with m.p. 91–93 °C. Mass spectrum: *m/z* 330, $(C_{12}H_{26}S_5)^+$ (not found); 268, $(C_{10}H_{20}S_4)^+$; 242, $(C_8H_{18}S_4)^+$; 208 $(C_8H_{16}S_3)^+$; 182 $(C_6H_{14}S_3)^+$. NMR ($CDCl_3$, $SiMe_4$ standard): $^1H$, δ 1.27 (t, 6 H, $J$ = 7.4), 2.58 (q, 4 H, $J$ = 7.4 Hz), 2.75 (m, 8 H), 2.78 (s, 8 H); $^{13}C$, 14.71 ($CH_3$), 25.96 ($CH_3\mathit{C}H_2$), 31.59 ($CH_3CH_2S\mathit{C}H_2$), 32.17 [$(\mathit{C}H_2SCH_2\mathit{C}H_2)_2S$].

(**CAUTION**: Although we have not experienced difficulty with the perchlorate salts described herein, readers are advised to exercise appropriate care when handling these potentially treacherously explosive salts.)

$[CuL]X_2$ ($X = ClO_4^-$ *or* $CF_3SO_3^-$). To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.0 mmol) in acetonitrile (3 $cm^3$) was added a solution of L (0.35 g, 1.06 mmol) in dichloromethane (5 $cm^3$). Reddish brown crystals formed immediately. After stirring for 30 min the crystals were collected, washed with dichloromethane and dried in air. Yield 0.49 g (83%). The product may be recrystallized from nitromethane by vapour diffusion of diethyl ether to induce precipitation, m.p. 152 °C (decomp.) (explodes!) (Found: C, 24.50; H, 4.25; Cu, 10.4. Calc. for $C_{12}H_{26}Cl_2CuO_8S_5$: C, 24.30; H, 4.40; Cu, 10.7%). The preparation of $[CuL][CF_3SO_3]_2$ was similar giving reddish brown crystals, m.p. 129 °C (decomp.) (Found: C, 24.10; H, 4.15; Cu, 9.6. Calc. for $C_{14}H_{26}CuF_6O_6S_7$: C, 24.25; H, 3.80; Cu, 9.2%).

$[Cu_2Cl_3L]$. To a solution of $CuCl_2 \cdot 2H_2O$ (0.34 g, 2.0 mmol) in acetonitrile (15 $cm^3$) was added a solution of L (0.33 g, 1.0 mmol) in dichloromethane (10 $cm^3$). The deep green solution was allowed to stand overnight by which time a reddish brown precipitate had formed which was collected, washed with acetone and dried in air. Yield 0.48 g (85%), m.p. 113 °C (decomp.) (Found: C, 25.90; H, 4.65; Cl, 17.60. Calc. for $C_{12}H_{26}Cl_3Cu_2S_5$: C, 25.55; H, 4.65; Cl, 18.85%).

$[NiL]X_2 \cdot H_2O$ ($X = ClO_4^-$ *or* $BF_4^-$). Solutions of Ni-

$(ClO_4)_2{\cdot}6H_2O$ (0.35 g, 1.0 mmol) in acetonitrile (10 $cm^3$) and L (0.50 g, 1.5 mmol) in dichloromethane (10 $cm^3$) were mixed and the resulting solution filtered. The filtrate was allowed to evaporate slowly at room temperature until a blue solid formed which was washed with dichloromethane and recrystallized from nitromethane by allowing diethyl ether vapour to diffuse into the solution until crystallization occurred. Yield 0.32 g (53%) (Found: C, 23.80; H, 4.00; Ni, 8.9. Calc. for $C_{12}H_{28}Cl_2NiO_9S_5$: C, 23.75; H, 4.10; Ni, 9.7%). The preparation of $[NiL][BF_4]_2{\cdot}H_2O$ was similar giving a blue powdery product. Yield 0.27 g (46%), m.p. 252 °C (decomp.) (Found: C, 25.15; H, 4.75. Calc. for $C_{12}H_{28}B_2F_8NiOS_5$: C, 24.80; H, 4.85%).

$[PdL][ClO_4]_2$. To a suspension of $PdCl_2$ (0.18 g, 1.0 mmol) in acetonitrile (15 $cm^3$) was added $AgBF_4$ (0.40 g, 2.0 mmol) in the same solvent (5 $cm^3$). The mixture was stirred for 30 min and the precipitate (AgCl) was removed by filtration. To the filtrate was added a solution of L (0.35 g, 1.1 mmol) in dichloromethane (5 $cm^3$) and a solution of sodium perchlorate (0.37 g, 3.0 mmol) in $H_2O$ (3 $cm^3$). The resulting purple solution was filtered and left standing at room temperature until a purple solid formed which was separated and washed with dichloromethane. Recrystallization was achieved from nitromethane by diffusion of diethyl ether vapour into the solution to initiate crystallization. Yield 0.41 g (64%) (Found: C, 23.80; H, 4.00; Pd, 16.1. Calc. for $C_{12}H_{26}Cl_2O_8Pd$: C, 23.75; H, 4.10; Pd, 16.7%). NMR ($CD_3CN$, $SiMe_4$ standard): $^1H$, δ 1.47 (t, 6 H, $J$ = 7.30 Hz), 2.95 (m, 2 H), 3.17 (m, 10 H), 3.30 (m, 4 H), 3.50 (m, 4 H).

*Crystal Structure Determinations of* $[CuL][ClO_4]_2$ *and* $[NiL(H_2O)][ClO_4]_2$.—*Crystal data.* $C_{12}H_{26}Cl_2CuO_8S_3$, $M = 593.09$, monoclinic, space group $P2_1/m$, $a = 11.677(4)$, $b = 10.602(2)$, $c = 18.841(3)$ Å, $\beta = 101.79(2)°$, $U = 2283(1)$ $Å^3$ (by least-squares refinement on diffractometer angles for 23 carefully centred reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.725$ g $cm^{-3}$, $F(000) = 1220$. Orange plate-like crystals. Crystal dimensions: 0.40 × 0.20 × 0.08 mm, μ(Mo-Kα) = 16.69 $cm^{-1}$.

$C_{12}H_{28}Cl_2NiO_9S_5$, $M = 606.25$, monoclinic, space group $P2_1/c$, $a = 10.223(2)$, $b = 18.647(2)$, $c = 12.593(3)$ Å, $\beta = 95.84(2)°$, $U = 2388.3(7)$ $Å^3$ (by least squares refinement on diffractometer angles for 20 carefully centred reflections, $\lambda = 0.710\,69$ Å), $Z = 4$, $D_c = 1.686$ g $cm^{-3}$, $F(000) = 1256$. Purple regular polyhedral crystals. Dimensions: 0.35 × 0.30 × 0.20mm.

*Data collection and processing.* Rigaku AFC6S diffractometer, ω–2θ mode with ω scan width $(1.21 + 0.30 \tan\theta)°$, ($[CuL][ClO_4]_2$) or $(1.31 + 0.30 \tan\theta)°$ {$[NiL(H_2O)][ClO_4]_2$}, ω scan speed 8.0° $min^{-1}$, graphite-monochromated Mo-Kα radiation; 3360 reflections measured ($2\theta_{max} = 45.0°$), 3181 unique ($R_{int} = 0.130$), absorption correction (max., min. transmission factors 1.00, 0.79) applied giving 1550 with $I > 2\sigma(I)$ ($[Cu(L)][ClO_4]_2$) or 4594 reflections measured ($2\theta_{max} = 50.0°$), 4343 unique ($R_{int} = 0.044$), absorption correction (max., min. transmission factors 1.00, 0.85) and secondary extinction (coefficient $0.559\,01 \times 10^{-7}$) applied giving 3117 with $I > 2\sigma(I)$ {$[NiL(H_2O)][ClO_4]_2$}.

*Structure analysis and refinement.* Direct methods followed by normal heavy-atom procedures with counting statistics weights. Full-matrix least-squares refinement with non-hydrogen atoms refined anisotropically (except for disordered perchlorate oxygens) and hydrogens in calculated positions. Final $R$ and $R'$ values $\{R = \Sigma||F_o| - |F_o||/\Sigma|F_o|, \quad R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}\}$ are 0.068 and 0.054 ($[CuL][ClO_4]_2$) and 0.051 and 0.056 {$[NiL(H_2O)][ClO_4]_2$}. Programs and computers used and sources of scattering factor data are given in ref. 18.

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

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