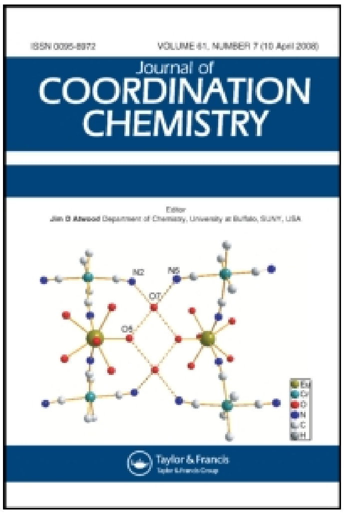

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# COMPLEXES OF BINUCLEATING LIGANDS. XIII. SOLUBLE COMPLEXES OF A LIGAND WITH A BRIDGING THIOPHENOXIDE COMPONENT AND PERIPHERAL n-OCTYL SUBSTITUENTS

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# COMPLEXES OF BINUCLEATING LIGANDS. XIII. SOLUBLE COMPLEXES OF A LIGAND WITH A BRIDGING THIOPHENOXIDE COMPONENT AND PERIPHERAL n-OCTYL SUBSTITUENTS

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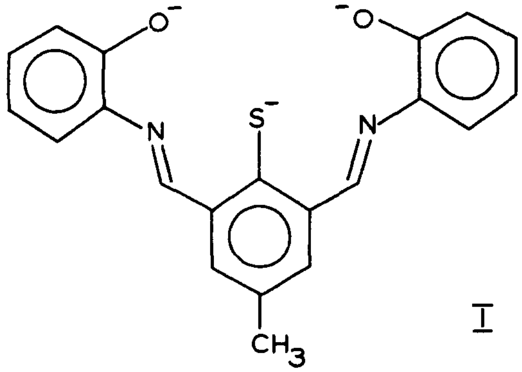
The trianionic binucleating ligands formally derived from the condensation products of S-n-octyldithiocarbazate with either 2-hydroxy- or 2-mercapto-5-methylisophthalaldehyde (hereafter $(L'')^{3-}$ and $L^{3-}$ respectively) gave the binuclear complexes $L''Ni_2(CH_3O)$, $L''Ni_2(C_6H_5CH_2O)$, $LNi_2(C_3H_3N_2)$, $LCu_2(C_3H_3N_2)$ and $LNi_2(SR)$ where $R = C_8H_{17}$ of $CH_3.C_6H_4$ and $C_3H_3N_2^- =$ the pyrazolate anion. These complexes were soluble in chloroform and $^1H$ n.m.r. data for some of them are presented. There was no evidence for significant magnetic exchange within $LCu_2(C_3H_3N_2)$. Attempts to generate $LNi_2(X)$ where $X^- = Cl^-$, $Br^-$ or $I^-$ gave $L_2Ni_3$ in which $L^{3-}$ fails to impose the intended molecular arrangement. Attempts to generate $L(Pd(II))_2(X)$ unexpectedly gave materials containing additional palladium, *i.e.* $LPd_4(CH_3CO_2)$ and $LPd_4(C_3H_3N_2)$.

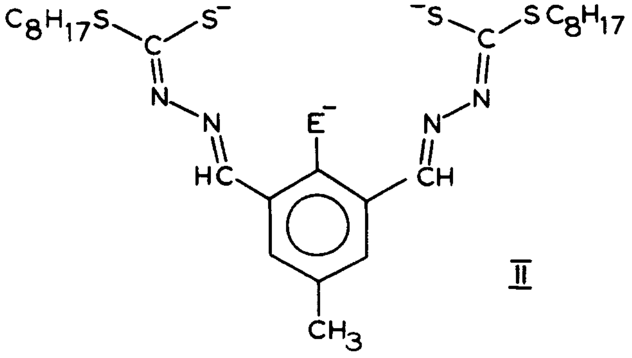
## INTRODUCTION

The trianionic binucleating ligand, I (hereafter referred to as $(L')^{3-}$), formally derived from 2-mercapto-5-methylisophthalaldehyde, was recently reported[1] to give a range of palladium(II) derivatives



I

of the general form, $L'Pd_2(X)$ or $[L'Pd_2(X)]^+Z^-$ depending on whether the bridging species, X, was anionic or neutral. The $L'Pd_2^+$ unit appeared to provide an exchangeable bridging site significantly larger than that in earlier binucleating systems with a bridging phenoxide component,[2] incorporating not only "two atom bridges" (*e.g.* Pd–N(O)$\overset{\cdots}{-}$O–Pd in $L'Pd_2(NO_2)$) and "one atom bridges" provided they were sufficiently large (*e.g.* Pd–I–Pd in $L'Pd_2I$) but also "three atom bridges" (*e.g.* Pd–NH$\overset{\cdots}{-}$C($C_6H_5$)-$\overset{\cdots}{-}$NH–Pd in $L'Pd_2(C_6H_5C(NH)_2)$) and even two independent species (*e.g.* in $[L'Pd_2(NO_2)_2]^-Na^+$). One of our long-term objectives in work of this sort is to generate complexes containing a range of different pairs of soft metal centres and to study the reactivity at the exchangeable bridging site therein. However, the suitability of $(L')^{3-}$ for this general purpose was cast in doubt by the high insolubility of the $L'Pd_2^+$ derivatives, which not only severely limited the structural information available (*e.g.* from n.m.r. spectra) regarding those complexes which could be obtained in pure form but also seriously hindered the isolation in a satisfactory state of purity of a number of other derivatives with potentially interesting species incorporated at the bridging site. The present work was undertaken with the aim of generating analogous systems containing peripheral substituents likely to increase the general solubility of the complexes. Both for reasons of synthetic convenience and because of the preference of soft metal centres for sulphur donors, we chose for this purpose the trianionic system II with $-E^- = -S^-$ (hereafter referred to as $L^{3-}$).



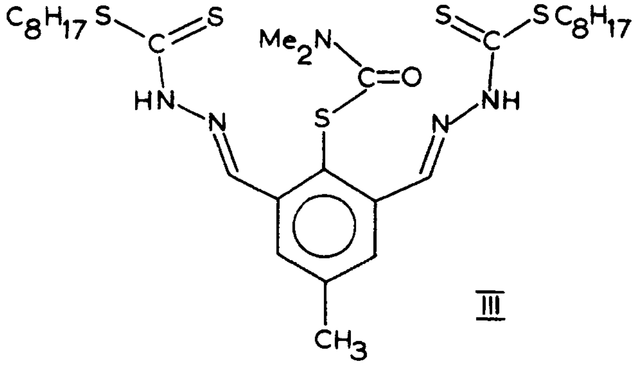
II

## RESULTS AND DISCUSSION

S-n-Octyldithiocarbazate was prepared by reaction of 1-bromo-n-octane with the dithiocarbazate ion.

Prior to embarking on the synthesis of complexes of $L^{3-}$ we isolated some complexes of the corresponding phenoxide-based ligand, II in which $-E^- = -O^-$ (hereafter $(L'')^{3-}$) in order to check quickly on the effectiveness of the octyl side-aims with regard to the solubilities of the derived complexes. Condensation of S-n-octyldithiocarbazate with 2-hydroxy-5-methylisophthalaldehyde gave $L''H_3$, which, with nickel(II) acetate in methanol, afforded $L''Ni_2(CH_3O)$. Reaction of $L''Ni_2(CH_3O)$ with benzyl alcohol gave crystalline $L''Ni_2(C_6H_5 \cdot CH_2O)$. Both these complexes showed promising solubilities in chloroform.

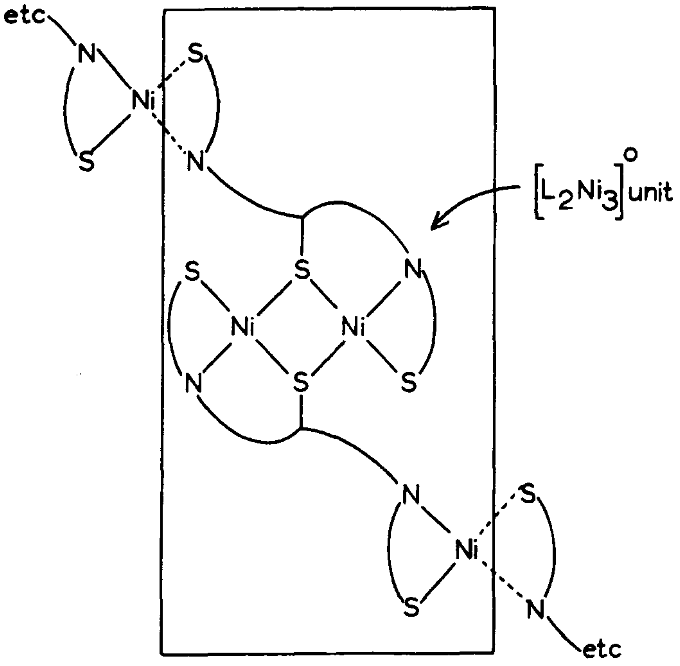
Condensation of S-n-octyldithiocarbazate with 2-(N,N-dimethylthiocarbamato)-5-methylisophthalaldehyde[1] gave III, which provided a convenient precursor to $L^{3-}$ being readily S-deprotected in the presence of metal ions. Reaction of III with nickel(II) bromide, lithium acetate and pyrazole in methanolic N,N-dimethylformamide at approximately 90°C gave $LNi_2(C_3H_3N_2)$. This green diamagnetic complex was readily soluble in chloroform in which solvent it showed a molecular weight by osmometry of 770 (Theor. 766). $LNi_2(C_3H_3N_2)$ was one of the first diamagnetic complexes of a binucleating ligand that we have been able to obtain which was sufficiently soluble to afford good quality n.m.r. data:– $^1H$ n.m.r. ($CDCl_3$–TMS) $\delta$ 7.96 (singlet, 2 imine protons), 7.28 (singlet, 2 aromatic protons), 7.06 (doublet, 2 pyrazole protons $\alpha$ to N's), 5.73 (multiplet, 1 pyrazole proton $\beta$ to N's), 3.13 (triplet, 4 methylene protons adjacent to S), 2.01 (singlet, 3 methyl protons of aromatic ring), 1.77 (multiplet, 4 methylene protons $\beta$ to S), 1.34 (broad, unresolved, 20 remaining methylene protons), 0.90 (triplet, 6 terminal methyl protons of octyl side chains). This spectrum is consistent with two atom bridging by the pyrazolate ion.



III

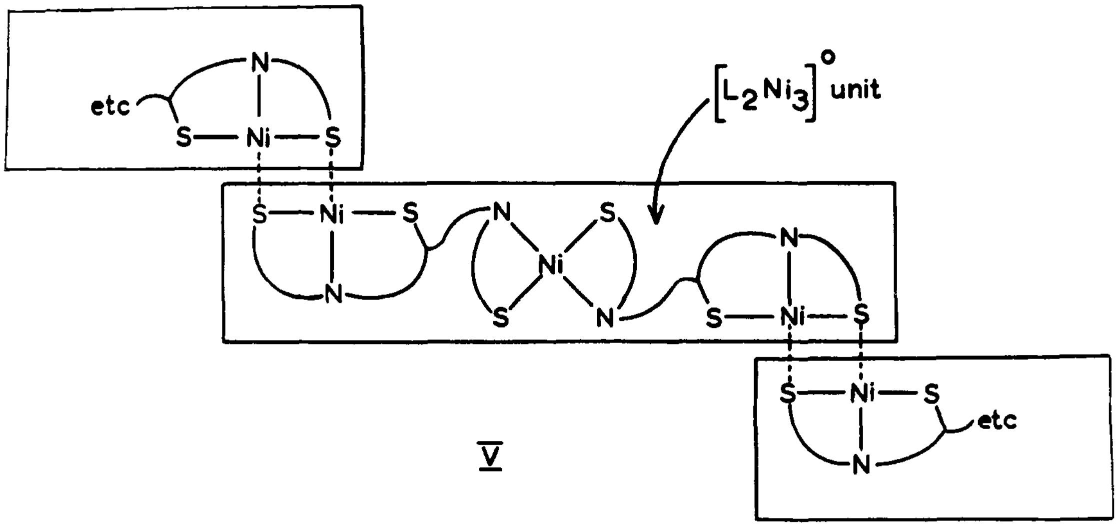
In the work with palladium derivatives of $(L')^{3-}$ the complex $L'Pd_2(CH_3CO_2)$, in which the acetate acted as a three atom bridge, proved to be a readily obtained and convenient starting material for the preparation of a wide range of derivatives, $L'Pd_2(X)$, by bridge exchange reactions.[1] Initial attempts to generate the analogous $LNi_2(CH_3CO_2)$ from reaction of III with nickel(II) acetate in N,N-dimethylformamide gave a red-brown crystalline material of composition $LNi_2(S \cdot C_8H_{17})$ in small yield. This result was quite reproducible with one particular sample of III, but reactions carried out subsequently under identical conditions with other samples of III consistently failed to give any $LNi_2(S \cdot C_8H_{17})$, despite the fact that the various samples of III had identical i.r. spectra. $LNi_2(S \cdot C_8H_{17})$ was readily soluble in chloroform:– $^1H$ n.m.r. ($CDCl_3$–TMS) $\delta$ 8.26 (singlet, 2 imine protons), 7.30 (singlet, 2 aromatic protons), 3.53 (triplet, 4 methylene protons of octyl groups $\alpha$ to S), 2.40 (singlet, 3 methyl protons of aromatic ring), ~1.8, ~1.3, ~1.2 (broad, unresolved, 24 methylene protons of $L^{3-}$ plus all 14 methylene protons of the bridging $C_8H_{17}S^-$), 0.90 (approx. triplet, 6 terminal methyl protons of $L^{3-}$ plus 3 terminal methyl protons of bridging $C_8H_{17}S^-$). The formation of a thiolate-bridged complex, $LNi_2(SR)$, was unexpected because, in earlier work with the $L'Pd_2(X)$ series,[1] we were unable to isolate complexes with $X^- = Cl^-$ or $RS^-$ and we took this failure to imply that the bi-metallic site was too large for bridging species of this size.

Attempts to prepare $LNi_2(CH_3CO_2)$ from those samples of III which did not lead to the formation of $LNi_2(S \cdot C_8H_{17})$ gave tarry products which we were unable to purify. Attempts to prepare $LNi_2(X)$, where $X^- = Cl^-$, $Br^-$ or $I^-$, from the appropriate nickel(II) halide, lithium acetate and III gave an almost black solid which, it emerged, was halide-free



IV

and had composition $L_2Ni_3$. This composition we take to imply that $L^{3-}$ is failing to impose the sort of binuclear structure that was intended. Structure IV, involving bridging by the thiophenoxide component of $L^{3-}$ but to a metal centre not attached to the same L unit and V, involving bridging by the terminal sulphur donors represent two feasible ways in which this composition might arise. Attention has been drawn previously to the strain inherent in binucleating systems with a bridging thiophenoxide and flanking imine-type side arms.[1] Presumably this strain in the intended $LM_2(X)$ arrangement is responsible for the adoption of the $L_2M_3$ composition if X is not a sufficiently good donor for M. Reaction of $L_2Ni_3$ with pyrazole gave $LNi_2(C_3H_3N_2)$ and with p-thiocresol gave $LNi_2(SC_6H_4CH_3)$ which



V

showed a $^1H$ n.m.r. spectrum analogous to that of $LNi_2(SC_8H_{17})$:– δ ($CDCl_3$–TMS) 8.29 (singlet, 2 imine protons), 7.34 (singlet, 2 aromatic protons), 8.08, 7.94, 7.06, 6.94 (AB quartet, 4 aromatic $S \cdot C_6H_4 \cdot CH_3$ protons), 3.11 (triplet, 4 methylene protons of $L^{3-}$ α to S), 2.42 (singlet, 3 methyl protons of central ring in $L^{3-}$, 2.26 (singlet, 3 methyl protons of $SC_6H_4CH_3$ unit), ~1.8 – ~1.1 with max. at 1.3 (broad, unresolved, remaining 24 methylene protons of $L^{3-}$), 0.92 (triplet, 6 terminal methyl protons of octyl side arms).

In many attempts to reproduce with the soluble $LNi_2(X)$ systems the diverse range of bridged species observed with the insoluble $L'Pd_2(X)$ systems[1] we were unable to isolate pure complexes (*e.g.* with $X^- = N_3^-$, $NO_2^-$, $C_6H_5N_3C_6H_5^-$, $(C_5H_4N)NH^-$, $(C_5H_4N)O^-$). Formation of intractable tars was a general problem in these reactions.

Reaction of III with cupric acetate in the presence of pyrazole in N,N-dimethylformamide gave $LCu_2(C_3H_3N_2)$ as a black crystalline solid which, like the nickel analogue, was soluble in chloroform. This complex is unusual in that cupric and thiolate ions are rarely compatible. In contrast to a number of pyrazolate-bridged di-cupric derivatives of phenoxide-based binucleating ligands which showed pronounced antiferromagnetic interactions within pairs of cupric centres,[3] there was no evidence for any significant magnetic exchange within $LCu_2(C_3H_3N_2)$ which showed Curie behaviour over the temperature range 120–296°K with an effective moment at room temperature of 1.76 B.M. The moleuclar weight of 885 (Theor. 776) observed by osmometry in chloroform perhaps indicates some degree of molecular association in solution, presumably via weak coordinate bonds between donor atoms in one molecule and metal centres in another. Several distinct differences between the i.r. spectra of $LCu_2(C_3H_3N_2)$ and $LNi_2(C_3H_3N_2)$ may also reflect the presence of this association in the solid copper complex and its absence in the solid nickel complex.

In investigations of the palladium(II) derivatives of $L^{3-}$ we failed completely to reproduce the chemistry observed in the $L'Pd_2(X)$ series.[1] Thus, attempts to generate $LPd_2(CH_3CO_2)$ from III and $Pd(CH_3CO_2)_2$ gave amorphous solids which were never obtained in a completely pure state but which reproducibly contained close to four palladium centres per ligand, with composition close to $LPd_4(CH_3CO_2)$. This product showed in its i.r. spectrum $\nu_{OCO(asym)}$ at 1545 cm$^{-1}$ and $\nu_{OCO(sym)}$ at 1410 cm$^{-1}$, effectively identical to those observed for $L'Pd_2(CH_3CO_2)$.[1] The possibility that the product consisted of $LPd_2(CH_3CO_2)$ contaminated with the appropriate proportion of palladium metal was excluded by the fact that the solid could be dissolved in benzene and reprecipitated, after filtration of the benzene solution, by addition of petroleum ether to yield material retaining the $LPd_4(CH_3CO_2)$ composition. The integrity of the $LPd_4$ unit was further demonstrated in the reaction of $LPd_4(CH_3CO_2)$ with pyrazole which yielded a material, again not completely pure, but with composition close to $LPd_4(C_3H_3N_2)$.

The unusual behaviour of $L^{3-}$ towards palladium-(II) raises serious questions concerning the suitability of this particular ligand for our purposes. Moreover, the formation of $L_2Ni_3$ casts even more serious doubt upon the usefulness, for our long-term purposes, not only of $L^{3-}$ in particular, but also of binucleating ligands in general with a bridging thiophenoxide component and imine side arms, since we especially intend these ligands to be capable of imposing on soft metals the composition $LM_2(X)$ even when the bridging species X is some reactive intermediate not able significantly to assist $L^{3-}$ in holding the two metals in close proximity. However, no evidence for undesirable behaviour of these sorts was observed with $(L')^{3-}$ in which the terminal donors were oxygen atoms and it is possible that both the formation of $L_2Ni_3$ and the uptake of more than two palladium centres are associated with the terminal sulphur donors in $L^{3-}$. Therefore, although continued study of the coordination chemistry of $L^{3-}$ may well reveal further interesting complexes we are presently diverting our attention to the generation of related systems with terminal oxygen and nitrogen donors and solubilising peripheral substituents.

## EXPERIMENTAL

### *S-n-octyldithiocarbazate*

Hydrazine hydrate (6.8 ml) was added to a solution of tetraethylammonium hydroxide in methanol (250 ml, 0.49 M). Carbon disulphide (7.3 ml) was added with stirring under dinitrogen to the solution cooled in ice, at such a rate as to maintain the temperature below 6°C. When the addition was complete 1-bromo-n-octane (20.9 ml) was added likewise, maintaining the temperature below 6°C. After 1.5 hours the reaction mixture was filtered and the filtrate was evaporated under reduced pressure below 35°C. Water (100 ml) was added and the mixture was extracted with dichloromethane (3 x 70 ml). Removal of the dichloromethane under vacuum below 30°C gave a colourless solid residue which was recrystallised from petroleum ether (60–80°). The crystals were collected and dried under vacuum at room temperature. *Yield,* 9.4 g. *Anal. Calcd.* for $C_9H_{20}N_2S_2$: C, 49.0; H, 9.1; N, 12.7; S, 29.1. *Found*: C, 48.6; H, 9.1; N, 12.5; S, 28.9.

### $L''H_3$

A solution of 2-hydroxy-5-methylisophthalaldehyde[4] (0.58 g) in hot methanol (5 ml) was added with stirring to a solution of S-n-octyldithiocarbazate (1.55 g) in hot methanol (5 ml) and the mixture was maintained near the boiling point. The bright yellow solid which separated on cooling was collected and dried under vacuum at 80°C. *Yield,* 1.2 g. M.p. 166–8°C. *Anal. Calcd.* for $C_{27}H_{44}N_4OS_4$: C, 57.0; H, 7.8; N, 9.9; S, 22.5. *Found*: C, 57.1; H, 7.6; N, 9.9; S, 22.4.

### $L''Ni_2(OR)$, $R = CH_3$, $CH_2C_6H_5$

A solution of $L''H_3$ (0.70 g) in hot methanol-chloroform (1:1, 26 ml) was added to a solution of nickel acetate tetrahydrate (0.68 g) in hot methanol (18 ml). The dark brown solution was stirred at the boiling point for ½ hour. On cooling a red-brown solid separated which was collected and recrystallized from benzene. The red-brown crystals were dried under vacuum at 80°C. *Yield,* 0.55 g. M.p. 135–7°C. *Anal. Calcd.* for $C_{28}H_{44}N_4O_2S_4Ni_2$: C, 47.1, H, 6.2; N, 7,9. *Found*: C, 48.7; H, 6.1; N, 7.9.

A solution of $L''Ni_2(CH_3O)$ (0.30 g) in N,N-dimethylformamide (5 ml) and benzyl alcohol (5 ml) was heated on the steam bath for 10 minutes. The red-brown crystals which separated on cooling were collected, washed with benzyl alcohol and dried under vacuum at 80°C. *Yield,* 0.31 g. M.p. 140–2°C. *Anal. Calcd.* for $C_{34}H_{48}N_4O_2S_4Ni_2$: C, 51.7; H, 6.1; H, 7.1; S, 16.2; Ni, 14.9. *Found*: C, 51.7; H, 6.1; N, 7.1; S, 16.2; Ni, 15.1.

### *The S-protected ligand, III*

A solution of 2-(N,N-dimethylthiocarbamato)-5-methylisophthalaldehyde[1] (1.04 g) in the minimum volume of boiling ethanol was added with stirring to a solution of S-n-octyldithiocarbazate (1.82 g) in the minimum volume of hot ethanol and the mixture was heated at the boiling point for 10 minutes. The yellow solid which separated was collected, after the mixture had cooled, and was washed with methanol. The solid was recrystallized from N,N-dimethylformamide-methanol and was dried at 80°C under vacuum. *Yield,* 2.01 g. M.p., 240–2°C. *Anal. Calcd.* for $C_{30}H_{49}N_5OS_5$: C, 54.9; H, 7.5; N, 10.7; S, 24.4. *Found*: C, 54.7; H, 7,4; N, 10.7; S, 24.7.

### $LNi_2(C_3H_3N_2)$

To a filtered solution of nickel(II) bromide (0.52 g) and lithium acetate (0.35 g) in N,N-dimethylformamide (3 ml) and methanol (2 ml) heated on the steam bath was added III (0.50 g) in N,N-dimethylformamide (10 ml). The mixture was heated at approx. 90°C for 10 minutes. Pyrazole (0.13 g) was added and the solution was heated at 90°C for a further 15 minutes. Upon cooling the solution deposited green needles which were collected and recrystallised from benzene-petroleum ether. The crystals were dried under vacuum at 80°C. *Yield,* 0.44 g. M.p., 122–3°C. *Anal. Calcd.* for $C_{30}H_{44}N_6S_5Ni_2$: C, 47.0; H, 5.8; N, 11.0; S, 20.9; Ni, 15.3. *Found*: C, 46.8; H, 6.0; N, 11.0; S, 20.2; Ni, 16.0.

$LNi_2(C_3H_3N_2)$ could also be prepared from $L_2Ni_3$ (below). Pyrazole (0.010 g) was added to a solution of $L_2Ni_3$ (0.050 g) in N,N-dimethylformamide (3 ml) and the mixture was heated at 90°C for 10 minutes. On cooling the solution deposited green needles, 0.014 g, which showed an i.r. spectrum identical to that of the above analytically pure $LNi_2(C_3H_3N_2)$.

### $LNi_2(SC_8H_{17})$

This material was obtained only from one particular sample of III which, however, showed an i.r. spectrum identical to those of other samples of III which failed to give any $LNi_2(SC_8H_{17})$. To a hot filtered solution of nickel acetate tetrahydrate (0.189 g) in N,N-dimethylformamide (5 ml) was added a solution of III (0.147 g) in hot N,N-dimethylformamide (5 ml). After the mixture had been heated at 90°C for 15 minutes, boiling methanol (5 ml) was added. On cooling and standing overnight the solution deposited red-brown needles which were collected and recrystallised from benzene. *Yield,* 0.026 g. M.p., 72–4°C. *Anal. Calcd.* for $C_{35}H_{58}N_4S_6Ni_2$: C, 49.7; H, 7.0; N, 6.7; S, 21.6. *Found*: C, 48.9; H, 6.8; N, 6.6; S, 21.3.

### $L_2Ni_3$

To a hot filtered solution of nickel chloride hexahydrate (0.91 g) and lithium acetate (0.39 g) in

N,N-dimethylformamide (10 ml) was added III (1.0 g) in hot N,N-dimethylformamide (10 ml) and the resultant dark brown solution was heated at 90°C for 20 minutes. The black solid which separated on cooling was collected, washed with methanol and dried under vacuum at 80°C. *Yield,* 0.60 g. M.p., 112–115°C. *Anal. Calcd.* for $C_{54}H_{82}N_8S_{10}Ni_3$: C, 48.2; H, 6.6; N, 8.3; S, 23.8; Ni, 13.1. *Found*: C, 48.7; H, 6.2; N, 8.6; S, 23.4; Ni, 13.1.

### $LNi_2(SC_6H_4 \cdot CH_3)$

p-Thiocresol (0.25 ml) was added to a stirred solution of $L_2Ni_3$ (0.074 g) in N,N-dimethylformamide (2 ml) and the mixture was heated on the steam bath for 20 minutes. Upon cooling the solution deposited red-brown needles which were collected and recrystallised from petroleum ether (80–100°C). *Yield* after drying in vacuum at 80°C, 0.040 g. M.p., 143–5°C. *Anal. Calcd.* for $C_{34}H_{48}N_4S_6Ni_2$: C, 49.6; H, 5.9; N, 6.8; S, 23.4; Ni, 14.3. *Found*: C, 49.2; H, 5.9; N, 7.0; S, 23.5; Ni, 14.8.

### $LCu_2(C_3H_3N_2)$

A solution of III (0.50 g) in hot N,N-dimethylformamide (3 ml) was added to a solution of cupric acetate monohydrate (0.32 g) and pyrazole (0.052 g) in hot N,N-dimethylformamide (3 ml). After the solution had been heated at 90°C for 5 minutes an equal volume of boiling methanol was added. Upon cooling the solution deposited black plates which were collected and recrystallised from benzene-acetone. *Yield* after drying under vacuum at 80°C, 45%. M.p., 193–5°C. *Anal. Calcd.* for $C_{30}H_{44}N_6S_5Cu_2$: C, 46.4; H, 5.7; N, 10.8; S, 20.7; Cu, 16.4. *Found*: C, 46.5; H, 5.8; N, 10.5; S, 21.0; Cu, 15.9.

### *Palladium derivatives of* $L^{3-}$

A solution of III (0.20 g) in hot N,N-dimethylformamide (3 ml) was added to a solution of palladium acetate (0.29 g) in hot benzene (3 ml). The resulting solution was heated to the boiling point for 5 minutes and then boiling methanol (3 ml) was added. The yellow-brown solid which separated upon cooling was collected, washed with methanol and dried under vacuum at 80°C. *Yield,* 0.24g. M.p., 130–4°C. The product was not completely pure but had composition in fair agreement with the formulation $LPd_4(CH_3CO_2)$. *Anal. Calcd.* for $C_{29}H_{44}N_4O_2S_5Pd_4$: C, 32.6; H, 4.2; N, 5.3; S, 15.0; Pd, 39.9. *Found*: C, 31.3; H, 3.8; N, 4.7; S, 13.8; Pd, 38.7.

The above palladium complex (0.10 g) in hot N,N-dimethylformamide (1 ml) was added to pyrazole (0.008 g) in hot N,N-dimethylformamide (1 ml) and the mixture was heated at 90°C for 10 minutes. The resulting solution upon cooling gave a yellow-brown precipitate which was collected and recrystallised from benzene-methanol. *Yield,* 0.080 g. M.p., 155–8°C. Again, the product was not completely pure but had composition in fair agreement with the formulation $LPd_4(C_3H_3N_2)$. *Anal. Calcd.* for $C_{30}H_{44}N_6S_5Pd_4$: C, 33.5; H, 4.1; N, 7.8; S, 14.0; Pd, 39.6. *Found*: C, 32.1; H, 3.8; N, 7.7; S, 13.8; Pd, 38.8.

### *Physical Measurements*

I.r. spectra were recorded on a Perkin–Elmer 457 Spectrophotometer with samples in KBr discs. N.m.r. spectra were recorded using a Varian HA–100 spectrometer. Molecular weights were determined using a Hitachi–Perkin Elmer Model 115 osmometer.

### *Analyses*

Analyses were performed by the Australian Microanalytical Service.

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