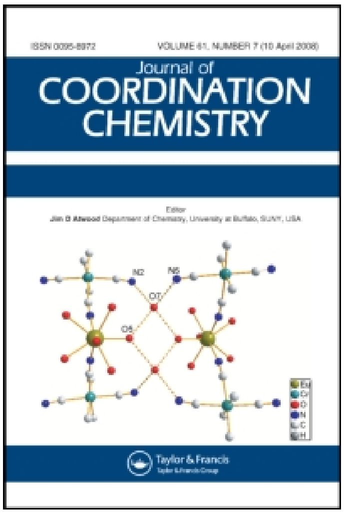

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COMPLEXES OF BINUCLEATING LIGANDS. X. SOME COPPER(II), NICKEL(II), PALLADIUM(II), AND PLATINUM(II) COMPLEXES OF SULPHUR-CONTAINING LIGANDS

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COMPLEXES OF BINUCLEATING LIGANDS. X. SOME COPPER(II), NICKEL(II), PALLADIUM(II), AND PLATINUM(II) COMPLEXES OF SULPHUR-CONTAINING LIGANDS

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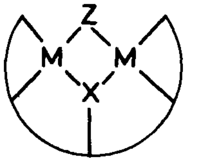
Copper(II) and nickel(II) complexes of the trianionic binucleating ligand (R^{3-}) derived from 4-hydroxy-*bis*-3,5-[N-(S-methyl-dithiocarbamate) formimidoyl] toluene have the general form $RM_2(Z)$ where Z represents a range of monoanionic bridging species. Palladium(II) and platinum(II) complexes formed by R^{3-} and the related trianionic ligands derived from 2-hydroxy-5-methylisophthalaldehyde di-2′-mercaptoanil and 2-hydroxy-5-methyliso-phthalaldehyde dithiosemicarbazone have the 2:1 formulation [(ligand)M_2(Z)] only when the bridging species, Z, coordinates strongly enough to give the binucleating ligand substantial assistance in maintaining the binuclear structure. In the absence of a "good" bridging group and in the presence of pyridine, 3:2 complexes of the form [(ligand)$_2$ M_3 (pyridine)$_2$] (where M = Pd, Pt) are produced in which the binucleating ligand fails to bind the two metals in close proximity.

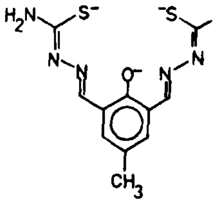
INTRODUCTION

Binucleating ligands containing soft donor atoms are of interest because they may be capable of binding two soft metal centres in close proximity



I

as in I, possibly allowing thereby the study of potentially novel chemistry at the bridging site. As a preliminary to such studies with new ligands we have found it useful to examine the derived nickel(II) and copper(II) complexes to determine whether or not the ligands do impose the expected binuclear structure and to obtain some indication of the spatial requirements of the bridging site. A range of copper(II) and nickel(II) complexes of the two sulphur sulphur-containing trianionic ligands II(hereafter Q^{3-}) and III(hereafter L^{3-}) prepared and studied for this purpose have been previously described.[1] Generally the complexes were of the form LM_2Z and QM_2Z, where Z represents a range of monoanionic species,



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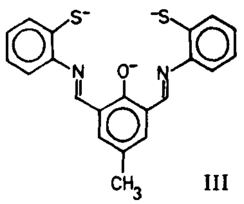
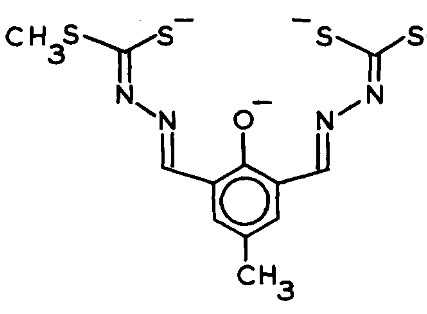


III

with structures basically as in I. A serious practical drawback associated with these two ligands with regard to the proposed extension to complexes of soft metals and reactivity studies thereon was the general insolubility of the derived complexes in common solvents, which leads to difficulties in purifying materials and in conducting solution work such as physical measurements and reactivity studies.



IV

The new ligand IV (hereafter R^{3-}) derived from 4-hydroxy-*bis*-3,5-[N-(S-methyl-dithiocarbamate)-formimidoyl] toluene (RH_3) has been prepared in the hope that the derived complexes may have more favourable solubility characteristics than those of Q^{3-} or L^{3-} and the present report describes the preliminary examination of the copper(II) and nickel(II) complexes of this ligand. Also presented are the results of a preparative survey of the complexes formed by the three ligands Q^{3-}, L^{3-} and R^{3-} with palladium(II) and platinum(II). The original objectives of the palladium and platinum work were (a) to establish that binuclear complexes of the type I could be formed with these soft metals and (b) to try to extend the range of bridging species to include potentially more interesting entities such as diazenes and acetylenes.

RESULTS AND DISCUSSION

Copper(II) and Nickel(II) Complexes of R^{3-}

The copper(II) and nickel(II) chemistry of R^{3-} paralleled very closely that reported previously for Q^{3-} and L^{3-} and discussion here is therefore much abbreviated. The complexes isolated are listed in Table I.

In general the complexes of R^{3-} were more soluble in solvents such as DMF, DMSO and pyridine than the complexes of Q^{3-} and L^{3-}, but to a disappointingly small extent. Those that were amenable to osmometry in pyridine gave the following molecular weights (concentrations in g/Kg in parentheses): $RNi_2(C_3H_3N_2)$, 511 (1.861), theoretical 554; $RNi_2(NH.C_4H_9)$, 572(1.298),

TABLE I
Analytical data for Cu(II) and Ni(II) complexes of R^{3-}

	%C		%H		%N		%S		%metal	
	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.
$RNi_2(OC_2H_5)$	33.9	34.1	3.4	3.5	10.5	10.5	24.1	24.2	22.1	22.2
$RNi_2(OC_2H_4OCH_3)$	34.1	34.2	3.8	3.6	9.7	9.9	22.8	23.0	20.9	21.1
$RNi_2(OCH_2C_6H_5)$	40.4	40.6	3.4	3.4	9.4	9.3	21.6	21.4	19.8	19.8
$[RNi_2]_2O$[a]	31.5	31.5	2.6	2.6	11.3	11.2	25.9	25.7	23.7	23.7
$RNi_2(SC_6H_4CH_3)$	39.4	39.6	3.3	3.6	9.2	9.5	26.3	25.9	19.3	19.4
$RNi_2(SH)$	30.0	30.2	2.7	2.6	10.8	10.6	30.8	30.9	22.6	22.6
$RNi_2(C_3H_3N_2)$[b]	34.7	34.7	2.9	2.9	15.2	14.9	23.2	22.9	21.2	21.6
$RNi_2(NH_2)$	31.1	31.0	3.1	3.0	13.9	13.6	25.5	25.7	23.4	23.7
$RNi_2(NHC_4H_9)$	36.6	36.8	4.0	4.2	12.5	12.7	23.0	22.7	21.1	21.4
$RNi_2(NHCH_2C_6H_5)$.DMF	41.5	41.4	4.2	4.3	12.6	12.4	19.3	19.6	17.6	18.1
$RNi_2(NC_4H_8)$[c]	36.6	36.8	4.0	4.2	12.6	12.2	23.0	22.6	21.0	20.8
$RNi_2(N_2H_3)$	30.1	30.3	3.1	3.3	16.2	15.7	24.8	24.4	22.7	22.7
$QNi_2(N_2H_3)$	29.0	28.7	3.1	3.2	24.6	24.9	14.2	14.0	25.8	25.6
$LNi_2(N_2H_3)$	48.1	48.0	3.5	3.7	10.7	10.6	12.2	11.9	22.4	22.2
$RNi_2(N_2H_2C_6H_5)$.DMF	39.6	39.6	4.1	4.0	14.7	14.4	19.2	19.2	17.6	18.1
$RNi_2(N_3)$	29.5	29.8	2.5	2.5	18.5	18.3	24.2	23.8	22.2	22.2
$RNi_2(NCO)$	31.8	31.5	2.5	2.4	13.2	13.0	24.2	24.0	22.2	21.9
$RNi_2(Cl)$.2DMSO[d]	30.1	30.4	3.7	3.5	8.3	8.4	28.3	28.2	17.3	17.6
$R_2Ni_4(SCN)$	31.4	31.8	2.7	2.5	12.2	12.4	28.0	27.6	22.8	22.5
$L_2Ni_4(SCN)$	49.4	49.3	2.9	3.0	6.7	6.6	15.4	15.3	22.5	22.5
$RCu_2(OC_2H_5)$	33.3	33.4	3.5	3.4	10.4	10.2	23.7	23.5	23.5	23.1
$RCu_2(OC_2H_4OCH_3)$	33.6	33.7	3.7	3.8	9.8	10.1	22.4	22.0	22.2	22.2
$RCu_2(OCH_2C_6H_5)$	39.8	40.1	3.4	3.3	9.3	9.3	21.2	21.2	21.1	21.1
$[RCu_2]_2O$[a]	30.9	30.8	2.6	2.7	11.1	11.1	25.4	25.3	25.2	25.1
$RCu_2(C_3H_3N_2)$[b]	34.1	34.0	2.9	2.8	14.9	14.7	22.8	22.6	22.5	22.4
$RCu_2(N_3)$	29.0	29.5	2.4	3.0	18.2	17.8	23.8	23.5	23.6	23.9
$RCu_2(NCO)$	31.2	31.6	2.4	2.7	13.0	12.6	23.8	23.7	23.6	22.7
$RCu_2(Cl)$.½DMSO[e]	29.4	29.8	2.8	2.6	9.8	9.9	25.3	25.2	22.3	22.2

[a] The oxide formulations are favoured over the hydroxide formulations, $RNi_2(OH)$ and $RCu_2(OH)$, which are also consistent with the observed compositions, because no OHst. band was apparent in the ir spectra. For comparison the ligand L^{3-} gave both an oxide $[LCu_2]_2O$, and a hydroxide, $LCu_2(OH)$, the latter showing a sharp OHst. band at 3493 cm^{-1}.[1]

[b] $C_3H_3N_2^-$ = pyrazolate anion.

[c] $NC_4H_8^-$ = conjugate base of pyrrolidine.

[d] %Cl: Calcd 5.2; found 5.1.

[e] %Cl: Calcd 6.2; found 6.4.

theoretical 558, $RNi_2(OC_2H_4OCH_3)$, 556(1.116), theoretical 562; $RNi_2(N_2H_2C_6H_5)$, 571(0.664), theoretical 594; $RCu_2(C_3H_3N_2)$, 537(1.593), theoretical 564; $RCu_2(N_3)$, 550 (0.852), theoretical 539; $RCu_2(OC_2H_5)$, 521(0.666), theoretical 542. In all the solutions used for osmometry the solutes behaved as non-electrolytes. These results provide support for the expected binuclear arrangements and all the properties of the complexes are consistent with structures of the basic type I.

All the nickel complexes, except $RNi_2(Cl)$.2DMSO were effectively diamagnetic, as were the alkoxide- and oxide-bridged copper complexes. The magnetic behaviour of $RNi_2(Cl)$.2DMSO closely paralleled that of $QNi_2(Cl)$.4DMSO[1], showing a room temperature moment of 2.3 B.M. averaged over all nickel present, consistent with one diamagnetic nickel(II) and one paramagnetic (3.2 B.M) nickel(II) per molecule. Complete removal of DMSO at 140°C under vacuum gave diamagnetic $RNi_2(Cl)$. The solvated compound showed Curie-Weiss behaviour in the range from room temperature to ca. 90°K with a Weiss constant of −33°. It appears that both DMSO molecules are coordinated to one nickel centre, rendering it six-coordinate and paramagnetic, whilst the other nickel centre remains four coordinate and diamagnetic. Removal of the DMSO then leaves all the nickel four-coordinate and diamagnetic. The nickel centres are probably in too close proximity to allow both to carry additional axial ligands, but it is not clear why the chloro-bridged complexes alone show this tendency to take on axial DMSO ligands. Attempts to attach the other monodentate donors, such as pyridine to $RNi_2(Cl)$ were unsuccessful, as they were with the $QNi_2(Cl)$.

The magnetic properties of the copper complexes are consistent with antiferromagnetic coupling within binuclear units, ranging from medium in $RCu_2(C_3H_3N_2)$ to very strong in the oxide and alkoxides. Only in the case of $RCu_2(C_3H_3N_2)$, for which the effective moment per copper varied from 1.34 B.M. at 290°K to 0.39 B.M. at 98°K, was the change in paramagnetism in this temperature range sufficient to warrant curve fitting to data calculated from the Bleaney-Bowers equation[2], which yielded the following values for the parameters 2J, g and T.I.P. respectively: 330 cm^{-1}, 2.1, 75 c.g.s. Effective moments for the other significantly paramagnetic copper complexes were as follows (in B.M.):-

$RCu_2(N_3)$, 0.88(293°K) to 0.12(126°K);
$RCu_2(Cl)$.½DMSO, 0.87(291°K) to 0.22(97°K);
$RCu_2(NCO)$, 0.80(290°K) to 0.40(99°K).

Their spectral bands arising from R^{3-} could generally be distinguished from those associated with the bridging species or with solvent molecules when present. All members of the series $RNi_2(Z)$, with the exception of $RNi_2(C_3H_3N_2)$, showed a common pattern of binucleating ligand bands. The basic pattern for $RCu_2(Z)$, the pyrazolate again being exceptional, was slightly but reproducibly different from that of the $RNi_2(Z)$ series, the difference being ascribable to different degrees of intermolecular axial interaction in the two series. Of the bridging groups examined pyrazolate is exceptional probably in that it alone yields a five-membered bi-metallic ring system $(\overline{\mathrm{M{-}N{-}N{-}M{-}O}})$ in contrast to the four-membered ring $(\overline{\mathrm{M{-}Z{-}M{-}O}})$ formed by all the others. It appears that the geometry of R^{3-} and therefore the associated ir pattern is much the same for a range of bridging species which are coordinated via a single atom whereas the pyrazolate bridge forces the side arms to open out to a larger extent leading to modification of the ir pattern. The common ir patterns for the $[RNi_2]^+$ and $[RCu_2]^+$ components in the ir spectra of $RNi_2(N_3)$ and $RCu_2(N_3)$ suggest bridging through a single N-atom and this receives independent support from the positions of the $\nu_{N_3(symm)}$ bands (1285 and 1280 cm^{-1} respectively), azide bands near 1300 cm^{-1} being reported as diagnostic of this bridging mode.[3] In the ir spectrum of $RNi_2(N_2H_3)$ the pattern associated with $[RNi_2]^+$ is the common one, again suggesting bridging through a single N, as in the other amido-bridged complexes, rather than through two adjacent N-atoms. In the earlier report[1] of complexes of Q^{3-} and L^{3-} the only one containing a hydrazine-derived bridging species was $QNi_2(N_2H_2C_6H_5)$. We have more recently isolated $QNi_2(N_2H_3)$ and $LNi_2(N_2H_3)$ in addition to $RNi_2(N_2H_3)$. These derivatives are of considerable significance with regard to the long-term objectives of generating species such as diazenes and dinitrogen at the bridging site, although it is recognised that nickel(II) is not an appropriate metal centre for attempts to oxidise the bridging hydrazine unit. The bridging species in $RNi_2(N_2H_2C_6H_5)$.DMF also appears to be bound via only one N-atom but we have no indication which of the two inequivalent atoms is coordinated. Whilst N-Hst. frequencies of the amido-bridging species were obscured by those of the binucleating ligand in the Q^{3-} series, they were observed, often as very sharp bands, in both the R^{3-} and L^{3-} series:- $RNi_2(NH_2)$, 3305(m); $LNi_2(NH_2)$[1], 3290(m), 3200(w); $RNi_2(NHC_4H_9)$, 3240(m); $LNi_2(NHC_4H_9)$[1], 3250(m); $RNi_2(NHCH_2C_6H_5)$, 3245(m); $LNi_2(NHCH_2C_6H_5)^1$, 3240(m); $RNi_2(N_2H_3)$, 3300(m), 3220(w), 3160(m); $LNi_2(N_2H_3)$, 3280(m), 3220(w), 3160(m); $RNi_2(N_2H_2C_6H_5)$.DMF, 3300(broad), 3160(shoulder); $LNi_2(N_2H_2C_6H_5)$, approximately 3220 cm^{-1} (ill-resolved and broad).

In view of the ready isolation of azido- and cyanato-bridged complexes with both copper(II) and nickel(II) derivatives of either R^{3-}, Q^{3-} or L^{3-}, our repeated failure, with any of these possible combinations, to incorporate directly a bridging thiocyanate group is surprising. However, materials which may contain indirectly generated thiocyanate were obtained by accident from attempts to incorporate thiourea at the bridging sites of $[RNi_2]^+$ and $[LNi_2]^+$. To date we have failed, despite repeated attempts, to isolate any complex containing a neutral bridging group such as thiourea, ethylene thiourea, pyridine N-oxide or pyridazine with trianionic binucleating ligands possessing C = N-linked side arms. Reaction between $RNi_2(OC_2H_5)$ and excess thiourea in DMF yielded an insoluble brown crystalline product consistently of composition in agreement with the formulation $R_2Ni_4(SCN)$. A product of analogous composition, i.e., $L_2Ni_4(SCN)$, was obtained by reaction of LH_3 (this protonated form of L^{3-} was actually a bis-thiazoline[1]) with nickel acetate and thiourea in DMSO. Both these products showed a strong band at 2040 cm^{-1} in their ir spectra which may correspond to $\nu_{SCN\ asymm}$. It has long been known that thiourea can be isomerised in part to ammonium thiocyanate at elevated temperatures[4], but substituting thiourea in the reaction mixtures by ammonium thiocyanate failed to generate the same products. The above formulations require that, for charge balance, a fraction of the nickel be in an oxidation state lower than II e.g., one out of four nickels in the I state. However, the complexes were diamagnetic and therefore the formulations $R_2(Ni(II))_4(SCN)(OH)$ and $Q_2(Ni(II))_4(SCN)(OH)$ (or $R_4(Ni(II))_8(SCN)_2O$ and $Q_4(Ni(II))_8(SCN)_2O$) which are also in acceptable agreement with the observed elemental compositions seem more realistic. It appeared possible that, for reasons which were not clear to us, the presence of both SCN^- and OH^- were necessary for the formation of a stable polynuclear arrangement. However, attempts to generate $R_2Ni_4(SCN)$ from reaction mixtures in which a source of $[RNi_2]^+$ was provided with both SCN^- and OH^- yielded $[RNi_2]_2O$. The situation is further complicated by the fact that reaction of RH_3 with nickel acetate and thiourea in DMSO yielded $RNi_2(SH)$, a product we were unable to obtain directly from HS^-. The appearance of the hydrosulphide suggests the further possibility that the above "thiocyanate" products may have the formulations $R_2Ni_4(SH)(CN)$ and $Q_2Ni_4(SH)(CN)$ which would also be consistent with the observed elemented compositions. No ν_{SH}st. was apparent in the ir spectra of the two products, but nor was it apparent in the spectrum of $RNi_2(SH)$. With the Q series of compounds reaction conditions analogous to those above yielded no complexes containing thiourea-derived fragments e.g., reaction of $QNi_2(OC_2H_5)$.2DMF with thiourea in DMF, under conditions precisely analogous to those used to generate "$R_2Ni_4(SCN)$", yielded merely $QNi_2(OH)$.3DMF, the same product as was obtained if thiourea was omitted. The above reactions are suggestive of some novel type of binuclear complex-promoted decomposition of thiourea but much further work on a system which is clearly complicated would be required to establish this. The appearance of $RNi_2(SH)$ is reminiscent of the reported formation of a CH_3S^--bridged platinum(II) complex by the platinum-promoted decomposition of methylisothiourea[5].

Palladium(II) and Platinum(II) Complexes of R^{3-}, Q^{3-} and L^{3-}

The Pd(II) and Pt(II) complexes isolated are listed in Table 2. The only complexes sufficiently soluble for osmometry showed the following molecular weights (concs. in pyridine, g Kg^{-1}, in parentheses):- $RPd_2(N_3)$, 606(1.291), theoretical 624; $RPd_2(C_3H_3N_2)$, 631(0.983), theoretical 649; $QPd_2(SC_6H_4CH_3)$, 620(1.001), theoretical 643; $QPd_2(N_2H_2C_6H_5)$, 608(1.384), theoretical 627. In the solutions used for osmometry the solutes behaved as nonelectrolytes. There is no reason to suppose that the 2:1 complexes adopt a configuration any different from those of the nickel(II) complexes e.g., the patterns associated with the binucleating ligands in the ir spectra of the 2:1 complexes were virtually identical to those of the analogous nickel complexes.

The 2:1 complexes were obtained either by reaction of the protonated ligand with metal dichloride in the presence of base and an excess of the bridging species or by bridge exchange reactions. Platinum(II) complexes were more difficult to isolate than palladium(II) complexes and only a few were characterised despite many attempts with a wide variety of potential bridging groups under widely varied conditions.

$QPd_2(OH)$.DMA was obtained accidentally in

TABLE II
Analytical data for Pd(II) and Pt(II) complexes of R^{3-}, Q^{3-} and L^{3-}

	%C		%H		%N		%S		%metal	
	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.
2:1 Complexes										
$RPd_2(Cl)^b$	25.2	25.6	2.1	2.4	9.1	9.2	20.7	21.4	34.4	34.3
$RPd_2(N_3)$	25.0	24.8	2.1	2.0	15.7	15.3	20.5	20.6	34.1	34.3
$RPd_2(C_3H_3N_2)$	29.6	29.7	2.5	2.7	12.9	12.7	19.8	19.5	32.8	33.0
$RPd_2(SC_6H_4CH_3)$	34.0	33.8	2.9	3.0	7.9	7.5	22.7	22.3	30.2	30.2
$RPt_2(SC_6H_4CH_3)$	27.2	27.0	2.3	2.0	6.4	6.1	18.2	17.8	44.2	44.4
$QPd_2(Cl).DMSO^c$	24.6	24.7	2.7	2.6	13.3	13.0	15.2	14.8	33.4	33.0
$QPd_2(N_3)$.DMSO	24.4	24.1	2.7	2.7	19.7	19.3	15.1	14.7	33.2	32.9
$QPd_2(C_3H_3N_2)$.2DMSO	29.1	29.1	3.5	3.4	15.1	15.4	17.2	16.8	28.7	29.0
$QPd_2(SC_6H_4CH_3)$	33.6	33.1	2.8	2.6	13.1	13.0	15.0	14.7	33.1	33.4
$QPt_2(SC_6H_4CH_3)$	26.3	26.1	2.2	2.0	10.2	10.0	11.7	11.3	47.5	47.4
$QPd_2(N_2H_2C_6H_5)$	32.5	32.3	3.1	3.1	17.8	17.7	10.2	10.3	33.9	33.7
$QPd_2(I).DMA^{a,d}$	24.5	24.7	2.8	3.0	13.4	13.4	8.7	8.3	29.0	28.6
$QPd_2(OH).DMA^a$	29.6	29.2	3.5	3.2	16.1	15.7	10.5	10.7	35.0	35.3
$LPd_2(N_3)$	40.0	39.8	2.4	2.6	11.1	11.0	10.2	10.1	33.8	33.6
$LPd_2(C_3H_3N_2)$	44.0	44.3	2.8	2.8	8.6	8.6	9.9	9.6	32.5	32.8
$LPd_2(SC_6H_5)$	46.5	46.5	2.9	3.0	4.0	3.8	13.8	13.6	30.6	30.8
$LPt_2(SC_6H_5)$	37.0	36.7	2.3	2.3	3.2	3.2	11.0	10.8	44.6	44.5
$LPd_2(SC_6H_4CH_3)$	47.2	46.9	3.1	3.4	3.9	3.8	13.5	13.5	30.0	29.8
$LPt_2(SC_6H_4CH_3)$	37.8	38.1	2.5	3.1	3.2	3.1	10.8	10.7	43.8	43.6
3:2 Complexes										
$R_2Pd_3.2C_5H_5N$	35.5	35.7	3.0	3.1	11.5	11.5	21.1	20.7	26.2	25.9
$R_2Pt_3.2C_5H_5N$	29.2	29.6	2.5	2.7	9.4	9.5	17.3	17.0	39.5	40.0
$L_2Pd_3.2C_5H_5N$	50.8	50.6	3.3	3.5	6.9	7.0	10.4	10.6	26.0	25.8
$L_2Pt_3.2C_5H_5N$	41.8	41.6	2.7	2.7	5.6	5.4	8.6	8.4	39.1	38.7

[a] DMA = dimethylacetamide
[b] %Cl: Calcd 5.7; found 5.2
[c] %Cl: Calcd 5.6; found 5.9
[d] %I: Calcd 17.3; found 16.8

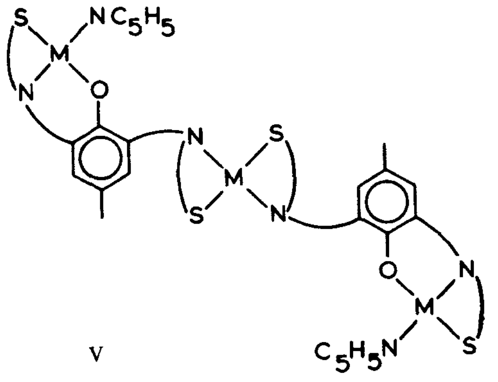
attempts to introduce a bridging cyano group by reaction of $QPd_2(N_3)$.DMSO with cyanide ion in undried dimethylacetamide. Under completely anhydrous conditions $QPd_2(OH)$.DMA was not obtained. The role of cyanide in this reaction is unclear. As in the copper(II) and nickel(II) series we were unable to isolate palladium(II) complexes incorporating thiocyanate at the bridging site.

The only hydrazine-derived complex of palladium(II) or platinum(II) that we were able to isolate was $QPd_2(N_2H_2C_6H_5)$. Attempts to oxidise the bridging unit in this complex with oxidants such as I_2, Br_2, Cu(II), benzoyl peroxide and various quinones were unsuccessful insofar as we were unable to isolate diazene products. The oxidation with I_2 yielded $QPd_2(I)$.DMA but neither this nor the analogous bromo-bridged complex could be obtained directly from reactions between ligand, Pd(II), base and the appropriate halide ion.

Many attempts to introduce a bridging acetylene unit, by treating the halo-bridged complexes first with Ag(I) followed by addition of the acetylene (e.g., pent-1-yne, phenylacetylene, diphenylacetylene) yielded intractable, often gummy products of variable composition showing no evidence for the presence of the acetylene.

Reaction of the azido-bridged palladium(II) complexes with the nitrosyl cation were studied in the hope either of generating dinitrogen[6] at the bridging site in an isolatable complex or, failing this, using the transient dinitrogen species as a labile starting material for the introduction of other bridging species e.g., acetylenes. In anhydrous DMSO, $NOClO_4$ reacted rapidly with $LPd_2(N_3)$ giving a red solution with gas evolution. Concentration of the solution by evaporation, addition of a variety of anions and the addition of precipitating solvents gave, in all cases, gummy or amorphous products of variable composition. Addition of acetylenes to the red solution followed by the same variety of workup procedures gave similar intractable products which showed no evidence for the incorporation of the acetylene. However, the red solution clearly contained the intact binucleating unit for crystalline binuclear complexes, e.g., $LPd_2(SC_6H_5)$ and $LPd_2(C_3H_3N_2)$, were readily isolated when a "good" bridging group was introduced.

When a small amount of pyridine was added to a DMSO solution containing RH_3(or LH_3), $PdCl_2$ (or $PtCl_2$) and lithium acetate-red crystalline products with the 3:2 formulation (Table 2) separated. These products were too insoluble for osmometry in all solvents tested. Reaction of the 3:2 complexes with thiols readily afforded the thiolate-bridged 2:1 complexes (e.g., this was the only way we could obtain $LPt_2(SC_6H_4CH_3)$ in pure state) indicating that R^{3-} and L^{3-} remain intact in the 3:2 complexes. Ir spectra showed marked differences from the very reproducible patterns observed for the 2:1 complexes of the same binucleating ligand, indicating a different ligand conformation. A very likely structure for the 3:2 complexes is V.



V

The results concerning Pd(II) and Pt(II) complexes reported here reveal a serious deficiency in the phenoxide-based ligands such as L^{3-}, Q^{3-} and R^{3-} with regard to their abilities to bind two soft metal centres in close proximity at the same time leaving a bridging site accessible to species which may not bind strongly to the two metals. It appears that the 2:1 binuclear structures of type I are formed with soft metals only if the bridging species Z (in I) gives the hard phenoxide donor substantial assistance in maintaining that structure; thus, the only 2:1 platinum(II) complexes we were able to isolate contained thiolate bridges which, no doubt, were mainly responsible for the 2:1 structure. The appearance of the 3:2 complexes of probable structure V in which the hard phenoxide donor has failed to impose the desired binuclear arrangement further emphasises this deficiency. It is likely that our failure to incorporate acetylenes at the bridging site is also related to this deficiency of the phenoxide-based ligands. The need for binucleating ligands containing a soft bridging system (e.g., $-X$ in I = $-S^-$) is clear and we are presently investigating synthetic approaches to ligands of this type.

EXPERIMENTAL SECTION

RH_3 – To a solution of potassium hydroxide (11.4 g) in 90% aqueous ethanol (70 cm^3) was added hydrazine hydrate (10 g) and the solution was cooled in ice. The temperature was kept below 6°C, and over a period of two hours, carbon disulphide (12.1 cm^3) diluted with ethanol (13 cm^3) was added with constant stirring. At the end of this period, pale yellow crystals of potassium dithiocarbazate were collected at the pump and dried by pressing. The compound was dissolved in 40% ethanol (40 cm^3) at room temperature and cooled in ice. Methyl iodide (29 g, about 12.8 cm^3) was slowly added with rapid shaking and the solution stirred until all cloudiness disappeared, the solution being allowed to warm up to room temperature. The solution was then cooled in ice for one hour when the white crystalline product, S-methyldithiocarbazate was filtered off. A further crop of crystals could be obtained on further cooling the filtrate. The crystals were dried at the pump. S-methyldithiocarbazate (4.0 g) was dissolved in 50% aqueous ethanol (100 cm^3) and 2-hydroxy-5-methylisophthalaldehyde (2.90 g) was dissolved separately in ethanol (300 cm^3). The solutions were heated to the boiling point, filtered, and the dialdehyde solution was added to the S-methyldithiocarbazate solution. On cooling, a yellow crystalline precipitate formed, which was filtered off and washed with copious volumes of ethanol. The product, RH_3, was dried at 60°C in vacuum. Yield, 6.1 g. *Anal.* Calculated for $C_{13}H_{16}N_4OS_4$: C, 41.9; H, 4.3: N, 15.1; 0, 4.3; S, 34.4; Found: C, 42.2; H, 4.4; N, 14.7; O, 4.2; S, 33.8%. The compound was used without further purification in the preparation of the complexes.

Preparation of Complexes

Cu(II) and Ni(II) complexes of R^{3-} were prepared by methods closely analogous to those given in ref. 1 for complexes of L^{3-} and Q^{3-}.

$RPd_2(Cl)$ – A solution of RH_3(2.7 g) and lithium acetate dihydrate (2.6 g) in DMSO (140 cm^3) at 90°C was added to a hot filtered solution of palladium chloride (3.5 g) in DMSO (140 cm^3). The resultant hot solution was filtered immediately, and allowed to cool to room temperature. On standing, red-brown crystals deposited which were collected, washed successively with DMSO, *p*-dioxane and diethyl ether and dried under vacuum at room temperature, yield 1.7 g.

$RPd_2(N_3)$ – A hot solution of RH_3 (0.38 g) and lithium acetate dihydrate (0.37 g) in DMSO (12 cm^3) and methanol (13 cm^3) was added dropwise to a filtered solution of palladium chloride (0.46 g) and sodium azide (1.6 g) in DMSO (20 cm^3). The red crystalline solid which formed was collected by filtration, washed successively with DMSO, *p*-dioxane, and diethyl ether and dried at room temperature under vacuum, yield 0.41 g.

$RPd_2(SC_6H_4CH_3)$ – A hot filtered solution of RH_3 (1.77 g) and lithium acetate dihydrate (2.50 g) and *p*-thiocresol (2.0 g) in DMSO (50 cm^3), was added to a hot filtered solution of palladium choride (1.77 g) in DMSO (50 cm^3). The red solution was heated on the steam bath until a red crystalline precipitate was deposited. The precipitate was filtered off from the hot suspension, washed successively with DMSO, *p*-dioxane and diethyl ether and dried at room temperature, under vacuum, yield 0.9 g.

$RPt_2SC_6H_4CH_3)$ – A solution at 90°C of RH_3 (1.77 g), lithium acetate dihydrate (2.50 g) and *p*-thiocresol (2.00 g) in DMSO (20 cm^3) was added to a hot filtered solution of platinum dichloride (2.00 g) in DMSO (20 cm^3). The solution was heated on the steam bath for 5 min, and on cooling, large red crystals formed. The product was collected, washed in the usual manner and dried under vacuum at room temperature, yield 0.7 g.

$RPd_2(C_3H_3N_2)$ – A hot solution of RH_3 (1.86 g) and lithium acetate tetrahydrate (2.50 g) and pyrazole (2.00 g) in DMSO (50 cm^3) and methanol (70 cm^3) at 70°C was added dropwise to a solution of palladium chloride (1.77 g) in DMSO (50 cm^3) at 90°C. The orange crystals which separated were collected, without first cooling the solution, washed with DMSO, then methanol, and dried at room temperature under vacuum, yield 1.1. g.

$R_2Pd_3.2C_5H_5N$ – Palladium chloride (2.00 g) and lithium acetate dihydrate (1.73 g) were dissolved in DMSO (80 cm^3) by heating on the steam bath. Solid RH_3 (2.00 g) was added in one amount to the solution, with stirring; the solution was quickly filtered, and hot pyridine (10 cm^3) was added. The solution was heated on the steam bath until orange crystals separated, which were collected at the pump, washed with pyridine and diethyl ether and dried at room temperature under vacuum, yield 0.91 g.

$R_2Pt_3.2C_5H_5N$ – Solid RH_3 (1.00 g) was added to a hot, filtered, solution of platinum dichloride (1.90 g) and lithium acetate dihydrate (1.50 g) in DMSO (100 cm^3). The hot solution was quickly filtered and hot pyridine (70 cm^3) was added. An orange-red microcrystalline precipitate formed on heating the solution on the steam bath. The solid was collected from the hot suspension, washed with pyridine and ether and dried at room temperature, yield 1.34 g.

$QPd_2(Cl).DMSO$ – Palladium chloride (0.18 g) was dissolved in DMSO (5 cm^3) at 90°C. The solution was then filtered and rewarmed to 90°C. To this solution, a filtered hot solution of QH_3 (0.16 g) and lithium acetate dihydrate (0.14 g) in DMSO (5 cm^3) and methanol (7 cm^3) was added dropwise. After the addition of about 10 cm^3 of the ligand solution, crystals began to separate from the red solution. The orange-red crystals were collected at the pump, washed with a small volume of 1:1 DMSO-methanol, then methanol, and dried at room temperature for 4 h, yield 0.11 g.

$QPd_2(N_3).DMSO$ – Suspended palladium chloride (0.46 g) and sodium azide (1.58 g) in DMSO (17 cm^3) slowly dissolved on heating on the steam bath. The solution was filtered and reheated. A hot, filtered solution of QH_3 (0.38 g) and lithium acetate dihydrate (0.37 g) in DMSO (12 cm^3) and methanol (17 cm^3) was added dropwise, until the deep red solution deposited dark red crystals of the product. The remainder of the ligand solution was slowly added with constant stirring, and the suspension was allowed to cool to room temperature. The crystals were collected, washed with DMSO, then methanol, and dried at 80°C under vacuum. Unlike most of the other complexes, $QPd_2(N_3)$.DMSO was readily recrystallized from hot DMSO without decomposition, yield 0.44 g.

$QPd_2(SC_6H_4CH_3)$ – A solution of QH_3 (0.16 g) and *p*-thiocresol (0.20 g) in DMSO (5 cm^3) at 80°C, was added to a filtered solution of palladium acetate (0.2 g) in DMSO (5 cm^3). Methanol was added drop-

wise until crystals began to form. The solution was then allowed to cool to room temperature. The product was collected, washed with DMSO, *p*-dioxane, then diethyl ether and dried at room temperature under vacuum, yield 0.08 g.

$QPt_2(SC_6H_4CH_3)$ – A solution of QH_3 (0.17 g), lithium acetate dihydrate (0.25 g) and *p*-thiocresol (0.2 g) in DMSO (2 cm^3) was added to a hot filtered solution of platinum dichloride (0.2 g) in DMSO (2 cm^3). The deep red solution was heated on the steam bath for 10 min then allowed to cool to room temperature, upon which red-brown crystals separated. The product was collected, washed with DMSO, *p*-dioxane and finally diethyl ether before drying under vacuum at room temperature.

$QPd_2(C_3H_3N_2).2DMSO$ – A hot solution of QH_3 (0.16 g), lithium acetate dihydrate (0.40 g) and pyrazole (0.20 g) in DMSO (5 cm^3) and methanol (6 cm^3) was added to a hot filtered solution of palladium chloride (0.25 g) in DMSO (5 cm^3). The orange crystalline precipitate which formed almost immediately was filtered off, washed with a small volume of DMSO, then with *p*-dioxane and dried at room temperature, under vacuum, yield 0.20 g.

$QPd_2(N_2H_2C_6H_5)$ – $QPd_2(N_3)$.DMSO (4.76 g) and lithium acetate dihydrate (1.45 g) were suspended in a 1:25 phenylhydrazine-DMA mixture (100 cm^3). The suspension was heated on the steam bath for 20 min. during which the suspended solid became red in colour. Without cooling, the product was collected, washed with DMA then ether, and dried at 80°C for 12 h, under vacuum, yield 4.0 g.

$QPd_2(I)$.DMA – $QPd_2(N_2H_2C_6H_5)$ (0.4 g) and lithium acetate dihydrate (0.13 g) were dissolved in a 0.1 *M* iodine solution in DMA (12 cm^3) by heating on a water bath, during which a gas was evolved. The hot solution was quickly filtered, and on cooling the filtrate deposited small orange crystals which were collected as usual, washed with DMA and dried at room temperature for 24 h under vacuum, yield 0.11 g.

$QPd_2(OH)$.DMA – $QPd_2(N_3)$.DMSO (0.4 g) and potassium cyanide (0.5 g) in DMA (10 cm^3) were heated for 40 min until all solid dissolved. The solution was filtered and on cooling and standing for 12 h the filtrate yielded large red crystals which effloresced in air. The crystals were collected, dried on filter paper and then quickly analysed. If the crystals were dried under vacuum, most, but not all, of the solvent DMA was lost, the last traces being held tenaciously.

$LPd_2(C_3H_3N_2)$ – LH_3 (0.085 g) was added to a hot solution of palladous chloride (0.1 g) and lithium acetate monohydrate (0.01 g) in DMSO (15 cm^3). The LH_3 dissolved to yield an intense red solution. A hot solution of pyrazole (0.061 g) in DMSO (5 cm^3) was then added, and after a few minutes the product separated as red-brown needles. After the reaction mixture had cooled, the product was collected, washed with DMSO and then methanol and dried in vacuum. Yield 0.115 g.

$LPd_2(N_3)$ – LH_3 (0.1 g) was added to a hot solution of palladous acetate (0.148 g) and sodium azide (0.137 g) in DMSO (10 cm^3), and an intense red solution resulted. Methanol at the boiling point was then slowly added until fine red crystals of the product began to separate. Addition of methanol was then ceased, and the reaction mixture set aside to cool and stand. The product was collected and washed with 1:1 DMSO-methanol and then methanol and dried in vacuum.

$LPd_2(SC_6H_5)$ – LH_3 (0.102 g) was added to a hot solution of palladous chloride (0.1 g) and lithium acetate monohydrate (0.124 g) in DMSO (40 cm^3) whereupon the LH_3 dissolved to yield an intense red solution. A hot solution of excess thiophenol in DMSO (2 cm^3) was then added. On warming, the resultant solution yielded glistening red crystals, which were collected from the hot suspension, washed with DMSO and then methanol and dried in vacuum. Yield 0.118 g.

$LPd_2(SC_6H_4CH_3)$ – was prepared in exactly the same way as $LPd_2(SC_6H_5)$ except that p-thiocresol was used in place of thiophenol.

$L_2Pd_3.2C_5H_5N$ – Pyridine (8 cm^3) was added to a hot solution of palladous chloride (0.2 g), lithium acetate monohydrate (0.173 g) and LH_3 (0.124 g) in DMSO (8 cm^3). The resultant intense red solution deposited fine red crystals after cooling and standing. The product was collected and washed with 1:1 DMSO-pyridine and then methanol and was dried in vacuum.

$L_2Pt_3.2C_5H_5N$ – Pyridine (2 cm^3) was added to a hot solution of platinum dichloride (0.315 g), lithium

acetate monohydrate (0.284 g) and LH_3 (0.3 g) in DMSO (2 cm^3). The resultant intense red solution after being warmed for about 5 minutes, yielded fine red needles. The product was collected and washed with 1:1 DMSO-pyridine and then methanol and was dried in vacuum.

$LPt_2(SC_6H_4CH_3)$ – A suspension of $L_2Pt_3.2C_5H_5N$ (0.050 g) in DMSO (5 cm^3) in the presence of excess *p*-thiocresol was warmed and stirred for 12 hours at 100°C. During this period the $L_2Pt_3.2C_5H_5N$ was replaced by fine red crystals of $LPt_2(SC_6H_4CH_3)$. The product was collected, washed with DMSO and was dried in vacuum. Yield 0.020 g.

$LPt_2(SC_6H_5)$ was prepared in the same way as $LPt_2(SC_6H_4CH_3)$ except that thiophenol was used in place of *p*-thiocresol.

PHYSICAL MEASUREMENTS

Ir spectra were recorded on a Perkin-Elmer 457 spectrophotometer as KBr discs or, for the observation of OHst. and NHst bands above 3000 cm^{-1}, as hexachlorobutadiene mulls. Magnetic moments were measured by the Gouy method using mercury cobalt(II) tetrathiocyanate as calibrant. Conductance measurements were made using a Philips PR 9500 bridge. Molecular weights were determined using a Hitachi Perkin-Elmer Model 115 apparatus.

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