A Novel Class of Dimeric Nickel(II) Compounds with Quadridentate Nitrogen Ligands: the Crystal Structure of $[Ni_2(C_{16}H_{16}N_6)_2]$

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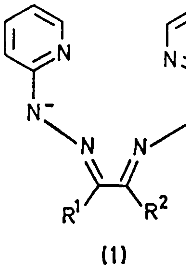
Summary The dianionic tricyclic quadridentate Schiff base ligands derived from 2-pyridylhydrazine and 1,2-diones form dimeric nickel(II) and palladium(II) species of a novel type, which apparently have a significant metal–metal bonding interaction, and which may be readily oxidised.

As part of a survey of the electrochemical properties of planar $[MN_4]$ compounds ($M = Ni^{II}, Pd^{II}$) we have investigated the compounds of (**1**).

In addition to $[ML]^{\circ}$, one example of which has previously been studied,[1,2] we have obtained soluble dimeric and insoluble polymeric compounds of both metals. The dimers $[M_2L_2]^{\circ}$ are red, diamagnetic compounds, with characteristic electronic spectra. They give well defined ^1H n.m.r. spectra, and undergo a variety of electrochemical oxidations and reductions.

Crystals of Ni_2L_2 {L = (**1**) for $R^1 + R^2 = [CH_2]_4$} from benzene were dark-red of empirical formula $\{Ni(C_{16}H_{16}N_6)\cdot C_6H_6\}$: monoclinic, $a = 9{\cdot}969(8)$, $b = 21{\cdot}765(10)$, $c = 19{\cdot}739(19)$ Å, $\beta = 102{\cdot}04(13^{\circ})$, $U = 4185(5)$ Å^3, $D_m = 1{\cdot}37$, $D_c = 1{\cdot}375$, $Z = 8$, group $P2_1/c$. The data were collected photographically (Weissenberg) and estimated visually (3065 independent reflections). The structure was solved by conventional Patterson and Fourier techniques, and refined by block-diagonal least-squares. R is 0·121 with anisotropic thermal motion for the nickel atoms and isotropic thermal motion for all remaining non-hydrogen atoms.

The unit cell contains four $[Ni_2(C_{16}H_{16}N_6)_2]$ units (Figure), together with four benzene molecules in general positions and four more lying across centres of symmetry. Each nickel atom is bonded, in an essentially planar array, to four nitrogen atoms, three of which are part of one quadridentate ligand, and the fourth, part of the other ligand. The configurations of the ligands are very different (Figure) from that in the monomeric species.[2] The central chelate ring has here expanded from a five- to a six-membered one, and the terminal pyridyl group bridges to the second nickel atom. Thus there are two N–C–N groups bridging the two nickel atoms. The co-ordination planes of the two metal atoms are inclined at 35° to one another.



(1)

The Ni–Ni distance of 2·81 Å is comparable with those (2·73—2·76 Å) found in three different thiol-bridged oligomeric nickel(II) species,[3] and distinctly less than that in [Ni(salen)]$_2$ (3·21 Å)[4] and [Ni(dmg)$_2$]$_n$ (3·25 Å)[5]. We believe there is significant metal–metal bonding.

TABLE

Half-wave potential data for some representative nickel compounds

	Compound	Electrode processes and half-wave potentials[a]			
		$+2 \leftrightharpoons +1$	$+1 \leftrightharpoons 0$	$0 \rightleftharpoons -1$	$-1 \rightleftharpoons -2$
NiL	$R^1 + R^2 = [CH_2]_4$	+0·52	+0·12	−1·31	−1·90[b]
”	$R^1 + R^2 = [CH_2]_5$	+0·60	+0·16	−1·34	−1·94[b]
Ni_2L_2	$R^1 + R^2 = [CH_2]_4$	+0·52[c]	+0·21	−1·51	−1·72[b]
”	$R^1 + R^2 = [CH_2]_5$	+0·60	+0·24	d	d

[a] In V *vs* S.C.E. (1M in LiCl), oxidation processes were measured with a rotating Pt electrode in CH_2Cl_2 (complex 0·3M) and reduction processes were measured with a dropping Hg electrode in dimethylformamide, the base electrolyte was $[Et_4N]ClO_4$ (0·05M) and the cell was at 20 °C, cyclic voltammetry was carried out using stationary Pt wire or Hg drop, all data were corrected for iR drop and the error was ±10 mV., and all processes were cyclically reversible unless otherwise stated. [b] Irreversible by cyclic voltammetry. [c] Further oxidation wave at +1·10 V. [d] No waves detected.

Voltammetric studies of the monomeric and dimeric compounds of nickel and palladium with (**1**) show that they undergo at least four electrode reactions (Table). The two oxidation and first reduction waves correspond to one-electron processes, and were reversible (cyclic voltammetry); the second reduction wave had i_d/c values twice that of the other three waves and may have been due to a two-electron process. The $E_{\frac{1}{2}}$ values, within both the monomeric and dimeric series of compounds depend on the nature of the central metal atom and on R^1 and R^2.

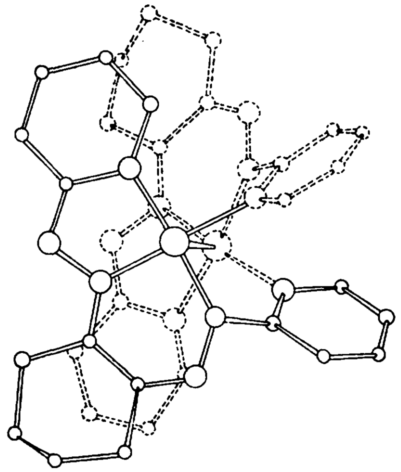


FIGURE *The structure of the* $[Ni_2(C_{16}H_{18}N_6)_2]$ *molecule. The large circles are nickel atoms and the smaller ones are carbon atoms.*

As might be expected from the potential data, oxidation of $[ML]^{\circ}$ and $[M_2L_2]^{\circ}$, to $[ML]^+$ and $[M_2L_2]^+$ respectively, is relatively easy. Indeed, treatment of $[Ni_2L_2]^{\circ}$ {L = (**1**), $R^1 + R^2 = [CH_2]_5$} with $AgPF_6$ in CH_2Cl_2 gave $[Ni_2L_2]PF_6 \cdot 2CH_2Cl_2$.

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