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Mechanism of formation of heteroleptic nickel(II)–arsine complexes from homoleptic precursors

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The reaction of square-pyramidal $[Ni(bdmma)_2]^{2+}$ {bdmma = bis[2-(dimethylarsino)phenyl]methylarsine} with either free pdma [*o*-phenylenebis(dimethylarsine)] or square-planar $[Ni(pdma)_2]^{2+}$ gave five-co-ordinate $[Ni(bdmma)(pdma)]^{2+}$. Kinetic studies (acidified 5% aqueous acetonitrile, 25.0 °C, $I = 0.30$ mol dm^{-3}, $LiClO_4$) showed that these processes involve the slow ($t_{\frac{1}{2}} = 105$ min) partial unravelling of a bdmma ligand from $[Ni(bdmma)_2]^{2+}$, followed by rapid ligand reorganization. The similar rearrangement involving $[Ni(bdmma)_2]^{2+}$ and square-planar $[Ni(tfpdma)_2]^{2+}$ [tfpdma = *o*-tetrafluorophenylenebis(dimethylarsine)] displays identical kinetic behaviour. In this medium the sequential addition of two pdma ligands to solvated nickel(II) to produce $[Ni(pdma)_2]^{2+}$ has second-order rate constants $k_1 = 680$ and $k_2 = 210$ dm^3 mol^{-1} s^{-1} respectively at 25.0 °C.

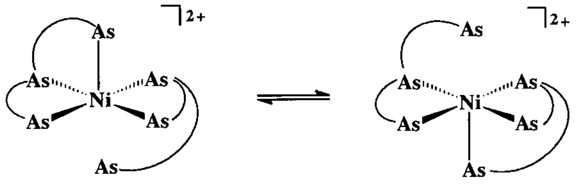
There are now a number of examples[1–4] of inter- and intra-molecular ligand-exchange processes occurring on nickel(II) complexes containing multidentate arsine ligands (As_n). Fluxionality in square-pyramidal $[Ni(As_3)(As_2)]^{2+}$ complexes is attributed to rapid intramolecular exchange of the bidentate As_2 ligand between equivalent donor sites,[3] and in five-co-ordinate $[Ni(As_3)_2]^{2+}$ {As_3 = bis[2-(dimethylarsino)phenyl]-methylarsine = bdmma} there is fast (NMR time-scale) internal exchange between terminal co-ordination sites, involving a bound $AsMe_2$ group of the tridentate ligand and the 'dangling' $AsMe_2$ group of the bidentate one,[1] Scheme 1. The latter process necessarily involves metal–ligand bond breaking. This is also seen in the slower (minutes) redistribution of chiral As_2 ligands from $[Ni\{(RR)\text{-}As_2\}_2]^{2+}$ and $[Ni\{(SS)\text{-}As_2\}_2]^{2+}$ which gives an equilibrium mixture of *meso* and racemic complexes.[4] Although little is known about the rates and mechanism of complexation of nickel(II) by arsenic donor ligands in the general sense, the latter result shows that intermolecular ligand transfer between nickel–arsine complexes is not unfavourable from the kinetic point of view. Herein we detail such transfer between square-pyramidal $[Ni(bdmma)_2]^{2+}$ and square-planar $[Ni(As_2)_2]^{2+}$ complexes [As_2 = *o*-phenylenebis(dimethylarsine) = pdma or *o*-tetrafluorophenylenebis(dimethylarsine) = tfpdma], equation (1). These processes are compared with that

$$[Ni(bdmma)_2]^{2+} + [Ni(As_2)_2]^{2+} \longrightarrow 2[Ni(bdmma)(As_2)]^{2+} \quad (1)$$

which occurs on direct reaction of $[Ni(bdmma)_2]^{2+}$ with free pdma, equation (2). As will be shown the (three) reactions are

$$[Ni(bdmma)_2]^{2+} + pdma \longrightarrow [Ni(bdmma)(pdma)]^{2+} + bdmma \quad (2)$$

linked by a common rate-determining step which involves a dynamic process occurring within the $[Ni(bdmma)_2]^{2+}$ reactant. As part of this investigation the kinetics of complexation of nickel(II) by pdma is also reported.



Scheme 1

Experimental

The complexes $[Ni(bdmma)_2][ClO_4]_2$,[5] $[Ni(bdmma)(pdma)][ClO_4]_2$,[6] $[Ni(pdma)_2][ClO_4]_2$[7] and $[Ni(tfpdma)_2][ClO_4]_2$[8] were prepared using published procedures. **CAUTION:** although we have not encountered difficulties with the above compounds, perchlorate salts are potentially explosive and should be treated with care. The compound pdma[9] was vacuum distilled [*ca.* 80 °C, 0.2 mmHg (*ca.* 27 Pa)] immediately before use: ^{1}H NMR (200 MHz, $CDCl_3$) δ, 7.37 (m, 4 H) and 1.21 (s, 6 H). The nickel content of hexaaquanickel(II) perchlorate (I.C.A.) was determined (> 96% purity) by inductively coupled plasma spectrometry and this material was used without further purification. Lithium perchlorate (Fluka, anhydrous) was used as received. Acetonitrile was dried over, and distilled from, CaH_2.

The complexes were insoluble in predominantly aqueous media, but a solvent suitable for kinetic studies was found to be 5% v/v aqueous acetonitrile made up to be 0.015 mol dm^{-3} in $HClO_4$† and maintained at $I = 0.30$ mol dm^{-3} ($LiClO_4$). A two-fold increase in $[H^+]$ did not alter the observed rates. The processes were monitored using either Cary 219 UV/VIS or Durrum D-110 stopped-flow spectrophotometers. The latter system incorporated a Harrick rapid-scan monochromator and was coupled to a Northstar Horizon computer running OLIS[10] software for data acquisition and processing.

Results and Discussion

The reaction of pdma with solvated Ni^{2+} ‡ was investigated under pseudo-first-order conditions, either with the metal ion in excess or present as the limiting reagent. In the former case the product had $\varepsilon = 335 \pm 15$ dm^3 mol^{-1} cm^{-1} at 440 nm independent of $[Ni^{2+}]$ {0.005–0.050, [pdma] = $(1.3\text{–}6.5) \times 10^{-4}$ mol dm^{-3}}, which contrasts with $\varepsilon_{440} = 1240$ dm^3 mol^{-1} cm^{-1} for $[Ni(pdma)_2]^{2+}$ (10^{-3} mol dm^{-3} solution). This suggests that the former value represents the absorption coefficient of the 1:1 complex (ε_{440} for solvated Ni^{2+} is 0.7 dm^3 mol^{-1} cm^{-1} in this system). Rate constants relating to the formation of [Ni-

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† Reaction rates were faster in the absence of added aqueous acid, but were not reproducible. Trace amounts of hydroxonickel species appeared to catalyse the processes, sometimes dramatically so.

‡ The nature of the solvated nickel(II) species is uncertain, but the UV/VIS spectrum indicates the co-ordination sphere includes both OH_2 and CH_3CN ligands.

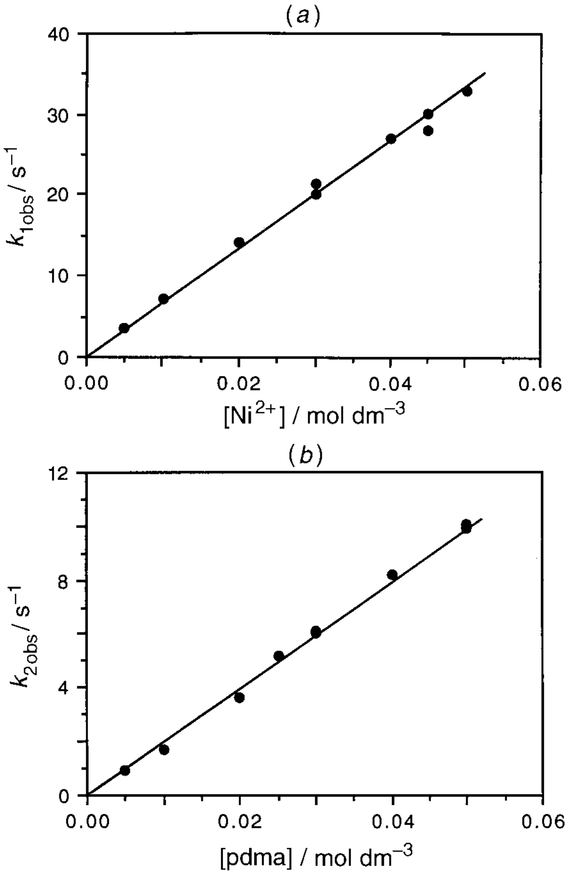

Fig. 1 Plots of k_{1obs} *versus* [Ni^{2+}] (*a*) and k_{2obs} *versus* [pdma] (*b*) for reaction of Ni^{2+} with pdma at 25.0 °C in 5% aqueous CH_3CN, [H$^+$] = 0.015, I = 0.30 mol dm^{-3} ($LiClO_4$)

(pdma)]$^{2+}$ are given as a plot of k_{1obs} *vs.* [Ni^{2+}] in Fig. 1(*a*); k_{1obs}/[Ni^{2+}] = k_1 = 680 ± 40 dm^3 mol^{-1} s^{-1}.

For [Ni^{2+}] = (1–2) × 10^{-4} mol dm^{-3} and with pdma in excess (0.005–0.050 mol dm^{-3}) complete conversion (>95%) to the orange-yellow bis(ligand) complex [Ni(pdma)$_2$]$^{2+}$ was found even at the lowest [pdma] condition. Kinetic traces showed a progressive increase in absorbance at all useful wavelengths (350–550 nm, rapid scan) and data (440 nm) were treated[11] on the basis that the reaction followed consecutive (pseudo) first-order kinetics, $Ni^{2+} \longrightarrow [Ni(pdma)]^{2+} \longrightarrow [Ni(pdma)_2]^{2+}$. For a particular [pdma] knowledge of the ε_{440} values for the individual nickel(II) species (see above), together with the computed value of the rate constant for the first step (k_{1obs} = 680 [pdma] s^{-1}), allowed the rate of formation of [Ni(pdma)$_2$]$^{2+}$ (k_{2obs}) to be established. Data are given in Fig. 1(*b*); k_{2obs}/[pdma] = k_2 = 210 ± 30 dm^3 mol^{-1} s^{-1}. Entry of the second pdma ligand into the co-ordination sphere of nickel(II) is thus three-fold slower than that of the first.§

Fig. 2 shows the spectral changes accompanying the reaction of the green [Ni(bdmma)$_2$]$^{2+}$ ion (6.0 × 10^{-4} mol dm^{-3}) with a slight excess of [Ni(pdma)$_2$]$^{2+}$ (6.6 × 10^{-4} mol dm^{-3}) to form red square-pyramidal [Ni(bdmma)(pdma)]$^{2+}$ at 25.0 °C [equation (1), As_2 = pdma]. Absorbance *vs.* time data (330, 440 and 540 nm) gave linear first-order plots, corresponding to k_{obs} = (1.2 ± 0.1) × 10^{-4} s^{-1} under this condition. Parallel behaviour was observed when [Ni(tfpdma)$_2$]$^{2+}$ was substituted for [Ni(pdma)$_2$]$^{2+}$ [equation (1), As_2 = tfpdma]. Product identity was established by spectral comparison using authentic [Ni(bdmma)(As_2)][ClO_4]$_2$ complexes [*e.g.* As_2 = pdma: λ_{max} 436 (ε 1500) and 535 nm (605 dm^3 mol^{-1} cm^{-1})]. A more comprehensive kinetic study (Table 1) showed that while both reactions were first order in [Ni(bdmma)$_2$$^{2+}$] they were independent of both the nature of the [Ni(As_2)$_2$]$^{2+}$ reagent (As_2 = pdma or tfpdma) and its concentration, provided this was in excess,¶ k = (1.1 ± 0.1) × 10^{-4} s^{-1}. Also, for reactant concentrations down to 1 × 10^{-4} mol dm^{-3} product formation was at least 95% complete. This implies that the equilibrium constant defined by equation (1) must be greater than (0.95 × 2 × 10^{-4})^2/(0.05 × 1 × 10^{-4})^2 = 1.4 × 10^3 at 25.0 °C and I = 0.30 mol dm^{-3} ($LiClO_4$). Clearly, [Ni(bdmma)(pdma)]$^{2+}$ is exceptionally stable relative to its homoleptic precursors. This may be due to entropic factors since the reaction increases the total number of chelate rings about the two metal centres from five to six, equation (1).

Table 1 Rate constants for the reaction of [Ni(bdmma)$_2$]$^{2+\,a}$ with [Ni(As_2)$_2$]$^{2+}$ (As_2 = pdma or tfpdma) complex ions at 25.0 °C, I = 0.30 mol dm^{-3} ($LiClO_4$), in 5% aqueous CH_3CN, [H$^+$] = 0.015 mol dm^{-3}

Reactant	10^4 [Ni(As_2)$_2$$^{2+}$]/mol dm^{-3}	10^4 k_{obs}/s^{-1}
[Ni(pdma)$_2$]$^{2+}$	1.33^b	1.13
	2.10	1.03
	2.37	1.15
	5.77	1.13
	10.0	1.13
[Ni(tfpdma)$_2$]$^{2+}$	1.34^b	1.15
	2.68^b	1.09
	3.83^c	1.12
	4.60^b	1.05

^{a} [Ni(bdmma)$_2$$^{2+}$] = 2 × 10^{-4} mol dm^{-3} unless otherwise stated. ^{b} [Ni(bdmma)$_2$$^{2+}$] = 0.85 × 10^{-4} mol dm^{-3}. ^{c} [Ni(bdmma)$_2$$^{2+}$] = 1.70 × 10^{-4} mol dm^{-3}.

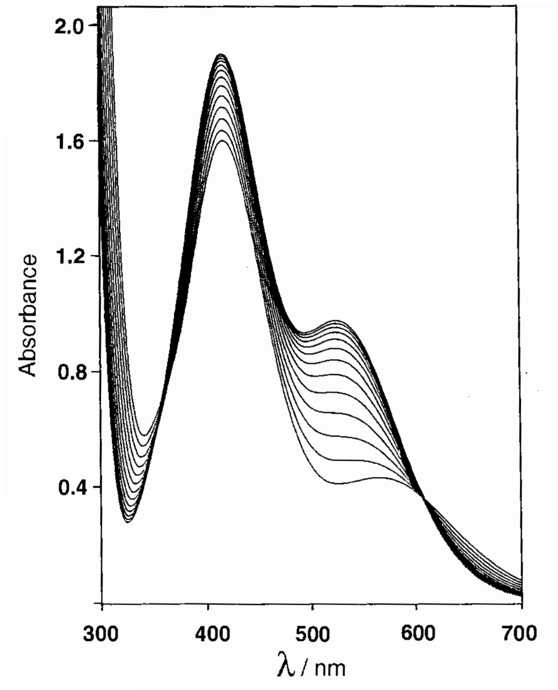

Fig. 2 Repetitive scan spectra (scan interval 25 min) for reaction of [Ni(bdmma)$_2$]$^{2+}$ (6.0 × 10^{-4} mol dm^{-3}) with [Ni(pdma)$_2$]$^{2+}$ (6.6 × 10^{-4} mol dm^{-3}) at 25.0 °C

Treatment of [Ni(bdmma)$_2$]$^{2+}$ with free pdma similarly results

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§ The relative rates of entry may reflect site availability; the first ligand may enter at any one of six co-ordination positions, whereas the second (to form the square-planar product) has the choice of only two. The values of the rate constants are, however, typical of those observed for reactions of Ni^{2+} with neutral bidentate ligands.[12]

¶ For reactions carried out using less than stoichiometric amounts of the square-planar complex the absorbance initially changed smoothly with time, apparently following a first-order course, but abruptly became time-independent once all the reagent had been consumed.

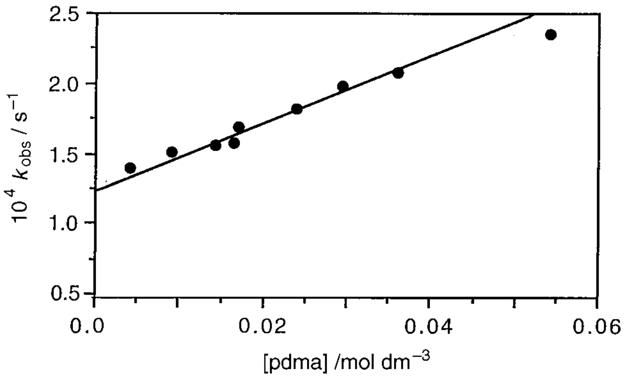
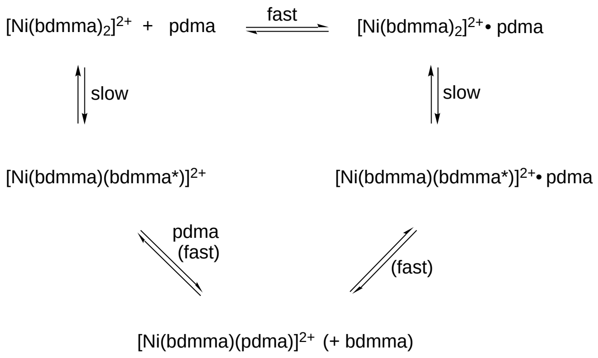


Fig. 3 Plot of k_{obs} *versus* [pdma] for reaction of $[Ni(bdmma)_2]^{2+}$ (6.0×10^{-4} mol dm^{-3}) with excess pdma at 25.0 °C in 5% aqueous CH_3CN, $[H^+] = 0.015$, $I = 0.30$ mol dm^{-3} ($LiClO_4$)



Scheme 2

in the production of $[Ni(bdmma)(pdma)]^{2+}$. Detailed kinetic studies of this process {437 nm, 25 °C, [pdma] = 0.00419–0.0543, $[Ni(bdmma)_2{}^{2+}] = 5.0 \times 10^{-4}$ mol dm^{-3}} showed that the mixed-ligand complex was fully formed at even the lowest [pdma]. The rate law contains both [pdma]-dependent and -independent contributions, Fig. 3, with k_{obs} varying according to equation (3), and $k_0 = (1.2 \pm 0.1) \times 10^{-4}\ s^{-1}$ and $k' = (2.0 \pm$

$$k_{obs} = k_0 + k'[\text{pdma}] \qquad (3)$$

$0.2) \times 10^{-3}$ $dm^3\ mol^{-1}\ s^{-1}$. The pdma-independent route must arise from a process involving solely the $[Ni(bdmma)_2]^{2+}$ reactant. Furthermore, the rate constant for this step has the same value (within experimental error) as those found for the similar reactions involving the $[Ni(As_2)_2]^{2+}$ species [equation (1)]. Since the terminal $AsMe_2$ groups of the ligands in $[Ni(bdmma)_2]^{2+}$ participate in fast intramolecular exchange (*ca.* $10^4\ s^{-1}$),[1] it appears that it is not the dissociation of these that is rate determining. We suggest that the slower process found here results from the further dissociation of the central AsMe group of the (momentarily) bidentate bdmma ligand. Such an event would produce an $[Ni(bdmma)(bdmma^*)]^{2+}$ intermediate (*cf.* Scheme 2) with at least one vacant (or solvent-occupied) co-ordination site available for pdma entry. The subsequent steps, involving co-ordination, chelate formation and loss of the now monodentate bdmma ligand, occur rapidly. The pdma-dependent pathway (above) presumably arises from a similar mechanism, but one involving preassociation of the reactants. The direct attack of pdma on five-co-ordinate $[Ni(bdmma)_2]^{2+}$ does not appear possible since its approach is blocked by the unco-ordinated $AsMe_2$ group. In the solid-state structure the latter is held in an octahedral position close (Ni–As *ca.* 380 pm) to the metal centre.[13] Molecular models suggest that this distance is near to the maximum for the complex in solution, since the structure is too rigid to allow a significant increase.

A comparison of the rates at which $[Ni(bdmma)_2]^{2+}$ reacts with pdma [*i.e.* k_0, equation (3)] and with $[Ni(pdma)_2]^{2+}$ and $[Ni(tfpdma)_2]^{2+}$ [$k = (1.1 \pm 0.1) \times 10^{-4}\ s^{-1}$ independent of reactant] clearly indicates that the intermediate described above is common to all three reactions and that its formation is overall rate determining. It is uncertain whether the subsequent reactions with the square-planar complexes involve intramolecular ligand redistribution from within dimeric species such as $[(bdmma)Ni(bdmma)Ni(As_2)_2]^{4+}$ (or equivalent structures). An equally likely possibility is that the $[Ni(bdmma)(bdmma^*)]^{2+}$ intermediate captures free As_2 produced by dissociation of $[Ni(As_2)_2]^{2+}$, and that ligand rearrangement occurs *via* separated metal centres. For equation (4) the equilibrium constant,

$$[Ni(pdma)]^{2+} + \text{pdma} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Ni(pdma)_2]^{2+} \qquad (4)$$

K, is less than $5 \times 10^4\ dm^3\ mol^{-1}$,[||] and consequently k_{-2} (= k_2/K, see above) > $210/(5 \times 10^4) = 4 \times 10^{-3}\ s^{-1}$. This is some 40-fold greater than the rate constant for formation of $[Ni(bdmma)(bdmma^*)]^{2+}$ ($1.1 \times 10^{-4}\ s^{-1}$, $t_{\frac{1}{2}} = 105$ min) so that free As_2 is generated fast enough to not limit the ligand-reorganization process.

In summary, this study shows that the unravelling of a bdmma ligand from the metal centre in $[Ni(bdmma)_2]^{2+}$ is rate determining in its replacement by other As_2 donors. We are now turning our attention to other nickel–arsine ligand-exchange reactions to see whether this type of process is of general significance.

[||] Serial dilution of $[Ni(pdma)_2]^{2+}$ in 5% aqueous acetonitrile shows that ε_{440} progressively decreases from 1240 (at 10^{-3}) to 320 $dm^3\ mol^{-1}\ cm^{-1}$ (at 1.2×10^{-5} mol dm^{-3}). We estimate at least 50% dissociation {to $[Ni(pdma)]^{2+}$} at $[Ni]_T = 4 \times 10^{-5}$ mol dm^{-3} whence $K < 5 \times 10^4\ dm^3\ mol^{-1}$.

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