

## An Unusually Extended Electron-transfer Series in Some Nickel Complexes with Innocent Homoleptic Arsine Coordination

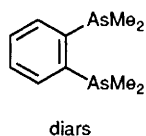
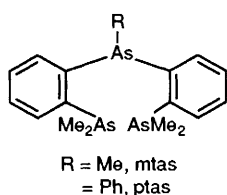
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Cyclic voltammetry in acetonitrile of the five-coordinate bis-triarsine complexes  $[\text{Ni}(\text{mtas})_2]^{2+}$  and  $[\text{Ni}(\text{ptas})_2]^{2+}$  [mtas = bis(2-dimethylarsinophenyl)methylarsine and ptas = bis(2-dimethylarsinophenyl)phenylarsine] reveals an extended metal-centred electron-transfer series with reversible formation of all nickel oxidation states from 0 to IV.

The higher oxidation states of nickel can be stabilised by bidentate As or P donor ligands incorporating the *o*-C<sub>6</sub>H<sub>4</sub> backbone. The ability of these ligands to stabilise Ni<sup>III</sup> and Ni<sup>IV</sup> arises from their strong  $\sigma$ -donor power, small steric requirements and their rigidity which resists dissociation from the metal.<sup>1-5</sup> On the other hand, Ni<sup>I</sup> and Ni<sup>0</sup> are stabilised by ligands which have strong  $\pi$ -acceptor properties and, when chelating, are sufficiently flexible to permit the geometrical changes which accompany the Ni<sup>II</sup>  $\rightarrow$  Ni<sup>I</sup>  $\rightarrow$  Ni<sup>0</sup> reductions.<sup>6-8</sup>



Herein is described the electrochemistry of  $[\text{Ni}(\text{mtas})_2]^{2+9}$  and  $[\text{Ni}(\text{ptas})_2]^{2+10}$ ,<sup>†</sup> which by cyclic voltammetry exhibit reversible formation of all oxidation states from Ni<sup>0</sup> to Ni<sup>IV</sup>. To our knowledge, these are the first nickel complexes to exhibit the complete metal-based electron-transfer series<sup>11</sup> and further, the Ni<sup>III</sup> and Ni<sup>IV</sup> complexes are the first to incorporate the homoleptic arsenic donor sets, NiAs<sub>5</sub> and NiAs<sub>6</sub>, respectively.

<sup>†</sup> X-Ray structural analyses<sup>10</sup> show that  $[\text{Ni}(\text{mtas})_2](\text{ClO}_4)_2$  and  $[\text{Ni}(\text{ptas})_2](\text{BF}_4)_2$  adopt distorted square-pyramidal and trigonal-bipyramidal structures, respectively. In both complexes only five sites are occupied by the two potentially tridentate ligands (Ni-As distances range from 2.28–2.47 Å), with a terminal -AsMe<sub>2</sub> group dangling uncoordinated at about 4 Å from the nickel. Variable-temperature <sup>1</sup>H NMR studies<sup>10</sup> indicate that, in both complexes, the dangling arsenic exchanges with some of the coordinated arsenic donors.

**Table 1** Electrochemical data<sup>a</sup>

Complex	$E^{\circ}$				Solvent
	i/0	ii/i	iii/ii	iv/iii	
[Ni(mtas) <sub>2</sub> ] <sup>2+</sup>	-1.16	-0.60	0.89	1.21	MeCN
[Ni(ptas) <sub>2</sub> ] <sup>2+</sup>	-1.10	-0.50	0.89	1.19	MeCN
[Ni(ptas) <sub>2</sub> ] <sup>2+</sup>	-1.26 <sup>b</sup>	-0.46	1.02	1.24	CH <sub>2</sub> Cl <sub>2</sub>
[Ni(diars)(mtas)] <sup>2+</sup>	-1.18	-0.66	1.02	1.38 <sup>b</sup>	MeCN
[Ni(diars)(mtas)] <sup>2+</sup>	-1.43 <sup>c</sup>	-0.54	1.16		CH <sub>2</sub> Cl <sub>2</sub>
[Co(mtas) <sub>2</sub> ] <sup>3+</sup>	-1.85	-0.61	0.04		MeCN

Ligand	$E_p^{ox(1)^d}$	$E_p^{ox(2)^d}$	Solvent
mtas	0.83	1.20	MeCN
ptas	0.91	1.24	MeCN
diars	1.08		MeCN

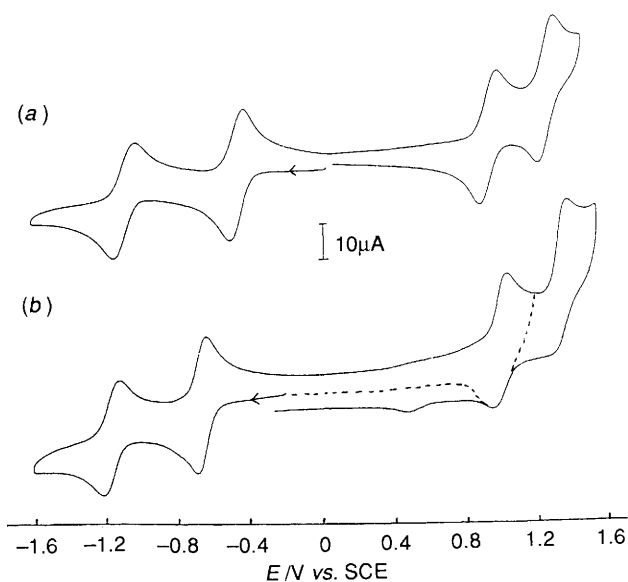
<sup>a</sup> Concentration  $10^{-3}$  mol dm<sup>-3</sup> complex or ligand; scan rate = 100 mV s<sup>-1</sup>, at a glassy carbon electrode of area 0.07 cm<sup>2</sup>. MeCN-0.1 mol dm<sup>-3</sup> [Bu<sub>4</sub>N]ClO<sub>4</sub> or CH<sub>2</sub>Cl<sub>2</sub>-0.1 mol dm<sup>-3</sup> [Bu<sub>4</sub>N]PF<sub>6</sub>, potentials in V vs. saturated calomel electrode (SCE) ( $E^{\circ}$  Fc<sup>+</sup>/Fc = 0.3 V). <sup>b</sup> Scan rate = 500 mV s<sup>-1</sup>. <sup>c</sup>  $T = -30^{\circ}\text{C}$ . <sup>d</sup> Peak potential for irreversible two-electron oxidation.

Cyclic voltammetry in MeCN-[Bu<sub>4</sub>N]ClO<sub>4</sub> of the five-coordinate bis-triarsine complexes [Ni(mtas)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> and [Ni(ptas)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> at room temperature and scan rates less than 1 V s<sup>-1</sup> shows, for each complex, a quasi-reversible oxidation step followed by a reversible oxidation, and a reversible reduction followed by a quasi-reversible reduction [Fig. 1(a) and Table 1]. All couples involve the transfer of one electron. ‡ To aid interpretation of these results, the electrochemistry of the five-coordinate triarsine-diarsine complex [Ni(diars)(mtas)](ClO<sub>4</sub>)<sub>2</sub><sup>12</sup> [diars = 1,2-bis(dimethylarsino)benzene] was also investigated since this complex does not contain a potential sixth As donor. Similar cathodic behaviour to the five-coordinate bis-triarsine complexes is observed but the second oxidation step is chemically reversible only at scan rates greater than 500 mV s<sup>-1</sup> or at lower temperatures [Fig. 1(b) and Table 1]. In the more weakly coordinating CH<sub>2</sub>Cl<sub>2</sub>-[Bu<sub>4</sub>N]PF<sub>6</sub> medium, [Ni(mtas)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> exhibits a reversible one-electron reduction followed by a reduction which is chemically reversible (and electrochemically quasi-reversible) only at scan rates greater than 200 mV s<sup>-1</sup> or at lower temperatures [Fig. 2(a)]. The anodic response is complicated by weak adsorption<sup>13</sup> but is qualitatively similar to that in MeCN-[Bu<sub>4</sub>N]ClO<sub>4</sub>. [Ni(mtas)<sub>2</sub>]<sup>2+</sup> (as the ClO<sub>4</sub><sup>-</sup>, BF<sub>4</sub><sup>-</sup> or PF<sub>6</sub><sup>-</sup> salts) is only sparingly soluble in CH<sub>2</sub>Cl<sub>2</sub> and could not be examined. For [Ni(diars)(mtas)](BF<sub>4</sub>)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>-[Bu<sub>4</sub>N]PF<sub>6</sub> the second reduction is chemically reversible only at temperatures below -30 °C (scan rate = 100 mV s<sup>-1</sup>) and only one oxidation is observed before the solvent limit [Fig. 2(b)].§

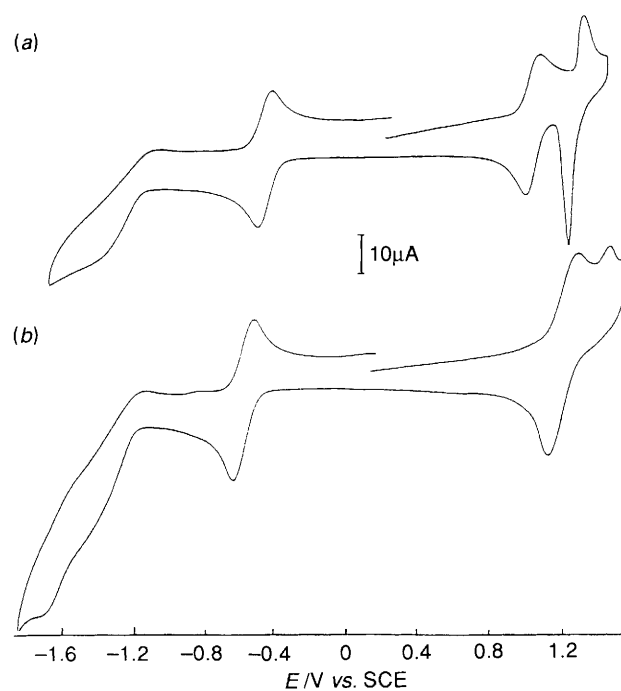
That the electron transfer processes are not isolated on the ligands is indicated by a number of observations. First, the instability of the products of the second reduction steps for [Ni(mtas)<sub>2</sub>]<sup>2+</sup> and [Ni(diars)(mtas)]<sup>2+</sup> in CH<sub>2</sub>Cl<sub>2</sub>-[Bu<sub>4</sub>N]PF<sub>6</sub> is consistent with the generation of Ni<sup>0</sup> species which react with the alkyl halide solvent.<sup>15</sup> Second, the free ligands cannot be reduced before the solvent limit and undergo chemically irreversible two-electron oxidations (Table 1). Further, the octahedral complex [Co(mtas)<sub>2</sub>]<sup>3+</sup><sup>14</sup> cannot be oxidised in MeCN-[Bu<sub>4</sub>N]ClO<sub>4</sub> and exhibits three reversible one-electron

‡ For reversible couples,  $\Delta E_p$  was the same as that for *in situ* ferrocene; for quasi-reversible couples,  $\Delta E_p$  was greater. Peak currents were  $\approx 90\%$  of those for equimolar *in situ* ferrocene.

§ The reversible oxidation is followed by a small peak of variable size and potential which we attribute to adsorption of a minor decomposition product.



**Fig. 1** Cyclic voltammetry in MeCN-0.1 mol dm<sup>-3</sup> [Bu<sub>4</sub>N]ClO<sub>4</sub>; scan rate = 100 mV s<sup>-1</sup>;  $T = 22^{\circ}\text{C}$ ; at a glassy carbon electrode (area = 0.07 cm<sup>2</sup>), of  $1 \times 10^{-3}$  mol dm<sup>-3</sup> solutions of (a) [Ni(ptas)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and (b) [Ni(diars)(mtas)](ClO<sub>4</sub>)<sub>2</sub>



**Fig. 2** Cyclic voltammetry in CH<sub>2</sub>Cl<sub>2</sub>-0.1 mol dm<sup>-3</sup> [Bu<sub>4</sub>N]PF<sub>6</sub> of (a)  $1 \times 10^{-3}$  mol dm<sup>-3</sup> [Ni(mtas)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> and (b)  $1.25 \times 10^{-3}$  mol dm<sup>-3</sup> [Ni(diars)(mtas)](BF<sub>4</sub>)<sub>2</sub>. Other conditions as in Fig. 1.

electron reductions which can reasonably be assigned to the formation of Co<sup>II</sup>, Co<sup>I</sup> and Co<sup>0</sup> species. Thus metal-based reductions are indicated for the nickel complexes. Considering the oxidation steps, it appears that the triarsine ligands cannot be oxidised when coordinated in a tridentate fashion and while oxidation of an uncoordinated arsine in complexes [Ni(mtas)<sub>2</sub>]<sup>2+</sup> and [Ni(ptas)<sub>2</sub>]<sup>2+</sup> must be considered, the observed reversible one-electron steps are not consistent with this interpretation. Finally, the electrochemistry of [Ni(diars)(mtas)]<sup>2+</sup> indicates significant participation of the metal centre. Six-coordination is the most likely geometry for the Ni<sup>IV</sup> centre<sup>15,16</sup> and for [Ni(ptas)<sub>2</sub>]<sup>2+</sup> this can be achieved by coordination of the dangling arsine to make use of all six As

donor atoms. For  $[\text{Ni}(\text{diars})(\text{mtas})]^{2+}$  with only five available As donors, MeCN or  $\text{ClO}_4^-$  may coordinate in the MeCN- $[\text{Bu}_4\text{N}]\text{ClO}_4$  medium to stabilize the  $\text{Ni}^{\text{IV}}$  oxidation state. However, in the absence of other donors, for example in the very weakly coordinating  $\text{CH}_2\text{Cl}_2-[\text{Bu}_4\text{N}]\text{PF}_6$  medium, the complex remains five-coordinate and the  $\text{Ni}^{\text{IV}}$  state becomes too unstable to be accessed.

Consideration of the  $E^{\circ'}$  values for successive electron transfers suggests that a change in coordination number occurs with the  $\text{Ni}^{\text{I}}-\text{Ni}^{\text{0}}$  step (five to four coordination) and with the  $\text{Ni}^{\text{III}}-\text{Ni}^{\text{IV}}$  step (five to six coordination).<sup>¶</sup> Chemically reversible oxidation of  $[\text{Ni}(\text{diars})(\text{mtas})]^{2+}$  in  $\text{CH}_2\text{Cl}_2-[\text{Bu}_4\text{N}]\text{PF}_6$  also implies a coordination number of five for the  $\text{Ni}^{\text{III}}$  species since no increase in coordination number is possible in this medium. On the basis of electron-transfer rates relatively slow structural rearrangements are indicated at the  $\text{Ni}^{\text{I}}-\text{Ni}^{\text{0}}$  and  $\text{Ni}^{\text{II}}-\text{Ni}^{\text{III}}$  steps. Details of these changes in coordination number and structure will be probed by further electrochemical and spectro-electrochemical studies. ||

Metal-based redox processes are now well-established for nickel complexes of phosphine and arsine ligands and are not unexpected for these complexes. However, the observation of the entire redox series from  $\text{Ni}^{\text{0}}$  to  $\text{Ni}^{\text{IV}}$  is unprecedented and can be attributed to the strong  $\sigma$ -donor and  $\pi$ -acceptor properties of the ligands and their 'moderate' flexibility which both stabilises the homoleptic  $\text{Ni}^{\text{III}}$  and  $\text{Ni}^{\text{IV}}$  complexes to ligand dissociation and permits the geometrical changes required in the formation of the  $\text{Ni}^{\text{I}}$  and  $\text{Ni}^{\text{0}}$  complexes. In addition, the tridentate ligands with their small cone angles at As are ideally suited to the generation of the  $\text{Ni}^{\text{IV}}$  complexes by allowing the incorporation of the remaining dangling arsine

group into the coordination sphere to give the unique  $\text{NiAs}_6$  donor set.

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<sup>¶</sup> Stabilisation of the product for an electron transfer by a change in coordination number makes the oxidation or reduction relatively easier than when no change accompanies electron transfer.

|| For the  $\text{Ni}^{\text{I}}-\text{Ni}^{\text{0}}$  step, slow charge transfer is consistent with structural change accompanying a change in coordination number. However, structural change does not necessarily lead to slow charge transfer<sup>17</sup> and slow charge transfer need not arise from a change in coordination number<sup>8</sup> hence the results for the oxidation steps are not self-contradictory.