

## Cyclic Voltammetric Study of a Series of Related Mono- and Binuclear Nickel Complexes of $\beta$ -Di- and $\beta$ -Triketonates and Their Diamine Schiff Bases

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The electrochemical behavior of several structurally related mono- and binuclear Ni(II) complexes has been investigated. The mononuclear complexes Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and Ni(acac)<sub>2</sub>en show quasi-reversible and reversible cyclic voltammograms, with  $E_{1/2}$  at -1.70 and -2.10 V vs. SSCE, respectively. The electrochemical reaction is a typical one-electron process in both cases. The binuclear Schiff-base complex Ni<sub>2</sub>(BAA)<sub>2</sub>en(py)<sub>2</sub> with Ni(II) in two different coordination environments exhibits only one quasi-reversible CV wave,  $E_{1/2} = -1.58$  V, corresponding to the nickel bound to four ketonate oxygens. No other electrochemical reaction takes place up to -2.3 V. The binuclear Ni(II) 1,3,5-triketionate Ni<sub>2</sub>(DBA)<sub>2</sub>(py) has two nearly reversible CV waves with  $E_{1/2}$  at -1.6 and -1.90 V. The fact that these are one-electron waves is confirmed by peak current calculations. The separation between the two Ni(II)/Ni(I) waves indicates a conproportionality constant of about 10<sup>5</sup>. Unlike the electrochemical behavior of the analogous binuclear Cu(II) compounds, there is no change in that of the Ni(II) compounds upon the addition of simple cations.

### Introduction

In previous papers<sup>1-4</sup> we have described the electrochemical properties of a series of binuclear Cu(II) 1,3,5-triketonates, the diamine Schiff-base derivatives of binuclear Cu(II) 1,3,5-triketonates, and a heterobinuclear Ni(II)-Cu(II) diamine Schiff-base 1,3,5-triketionate complex. In each case, one observes a reversible one-electron transfer in the potential range 0 to -1.8 V corresponding to Cu(II)  $\rightleftharpoons$  Cu(I). And in each case, the reduction of the second metal ion occurs at very much more negative potentials than that of the first and is not easily studied due to overlapping ligand electrochemical reactions. The difference between the two is on the order of 1 V. Addition of simple cations such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, etc. to the electrochemical cell (that also contains tetraethylammonium perchlorate as supporting electrolyte) has the abstruse effect of converting the observed one-electron transfer into a two-electron-transfer process in which the potentials for the transfer of the two electrons are almost identical. In addition, the cation causes a shift in the redox potential of the initial one-electron process vs. the resulting two-electron process of about +300 mV. Thus, the electrochemistry for these binuclear complexes in the presence of such cations is qualitatively and quantitatively different from that in their absence. The present work was undertaken in order to extend the electrochemical study of binuclear complexes to other metal ions and to further investigate the effect of cations on the electron-transfer processes.

### Experimental Section

**Ligands.** The  $\beta$ -polyketones 2,4-pentanedione (Hacac), 1-phenyl-1,3,5-hexanetrione<sup>5</sup> (H<sub>2</sub>BAA), and 1,5-diphenyl-1,3,5-pentanetrione<sup>5</sup> (H<sub>2</sub>DBA) have been described or, in the case Hacac, are readily available. The Schiff-base derivatives were prepared by the condensation reaction of the  $\beta$ -polyketone with a 5% excess of ethylenediamine in absolute methanol. These ligands are abbreviated H<sub>2</sub>(Acac)en and H<sub>4</sub>(BAA)<sub>2</sub>en.

**Synthesis of Complexes.** Preparation and characterization of the complexes have been reported. The mononuclear complexes are Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, Ni(acac)<sub>2</sub>en, and Ni[(HBAA)<sub>2</sub>en]-N<sub>2</sub>O<sub>2</sub><sup>6</sup> where N<sub>2</sub>O<sub>2</sub> indicates that the Ni(II) is bound to the imine nitrogens and the central enolate oxygens. The binuclear complexes are Ni<sub>2</sub>(DBA)<sub>2</sub>(py)<sub>4</sub><sup>7</sup> and Ni<sub>2</sub>(BAA)<sub>2</sub>en(py)<sub>2</sub>.<sup>8</sup>

**Electrochemistry.** Electrochemical experiments were carried out with a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a PAR Model 179 digital coulometer and Model 175 universal programmer. Data collection for scan rates faster than 100 V/s was accomplished with the Nicolet Model 2090-3C digital oscilloscope with pen output, disk recorder, and binary I/O. All electrochemical measurements were made in Omnisolv (MCB) *N,N*-dimethylformamide (DMF) that was used without further purification. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was purified by a chromatographic procedure developed in our laboratory.<sup>9</sup> The solutions were deoxygenated with ultrahigh-purity N<sub>2</sub> that had been passed through a chromous perchloric acid scrubber, a CaSO<sub>4</sub> drying column, and a DMF-TEAP solution. A three-electrode cell with a saturated NaCl calomel reference electrode (SSCE), a Pt-wire counter electrode, and Brinkmann Model EA290 hanging mercury drop (HMDE) or a Tacussel Pt disk working electrode was used in the cyclic voltammetry (CV). The reference electrode was separated from the sample chamber by two salt bridges. The bridge adjacent to the reference electrode contained a 0.13 M TEAP aqueous solution, and the one adjacent to the sample chamber contained a 0.1 M TEAP in DMF solution. Controlled-potential coulometry (CPE) was carried out at a stirred Hg pool or a Pt grid working electrode, with a counter electrode consisting of a Cu coil in a 0.10 M NaCl aqueous solution separated by a salt bridge containing 0.10 M TEAP in DMF.

### Results

In order to verify that the ligands are not involved in the electron-transfer processes of interest, the cyclic voltammograms of H<sub>2</sub>BAA and H<sub>4</sub>(BAA)<sub>2</sub>en were recorded. The first reduction for H<sub>2</sub>BAA in DMF at a HMDE is an irreversible process with a peak potential of -1.61 V. This potential does not vary in the scan rate range 0.20-100 mV/s. Under the same conditions, H<sub>4</sub>(BAA)<sub>2</sub>en exhibits an irreversible reduction at -1.97 V, which does not vary in the range 20-100 mV/s. Introduction of a base such as (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N does not change the results for either ligand.

For Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> with a HMDE a quasi-reversible CV wave occurs with  $E_{1/2}$  at -1.70 V corresponding to the Ni(II) to Ni(I) reduction. The cathodic wave for Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> is considerably broader than the anodic wave. The process appears totally irreversible with a Pt disk electrode. For Ni(acac)<sub>2</sub>en with the HMDE, on the other hand, a reversible, one-electron wave is observed with  $E_{1/2} = -2.10$  V. In the scan rate range 0.100-50.00 V/s the values of peak potential separation,  $\Delta E_p$ , and the cathode wave half-width,  $E_{pc} - E_{pc/2}$ , are 59 mV ( $\pm 6$  mV). The peak height ratios are very nearly equal to 1.0 throughout this scan rate range. Although the Ni(II) coordination environment in Ni(HBAA)<sub>2</sub>en-N<sub>2</sub>O<sub>2</sub> is the same as the Ni(II) in Ni(acac)<sub>2</sub>en, the electrochemical properties are quite different. Ni(HBAA)<sub>2</sub>en-N<sub>2</sub>O<sub>2</sub> exhibits two irreversible reduction waves with

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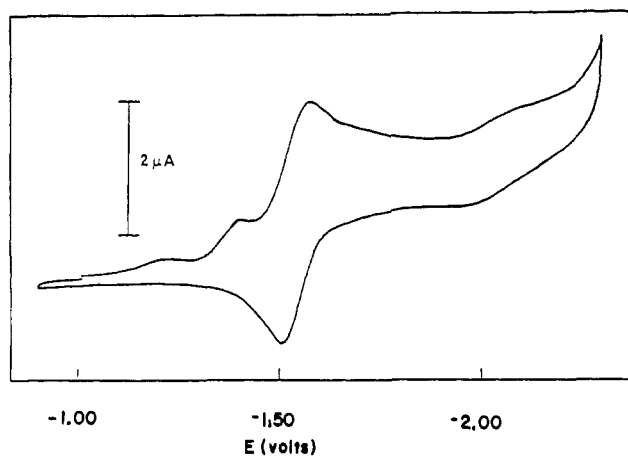


Figure 1. Cyclic voltammogram of  $1.004 \times 10^{-3}$  M  $\text{Ni}_2(\text{BAA})_2\text{en-CH}_3\text{OH}$  in DMF with 0.10 M TEAP at 0.050 V/s (HMDE).

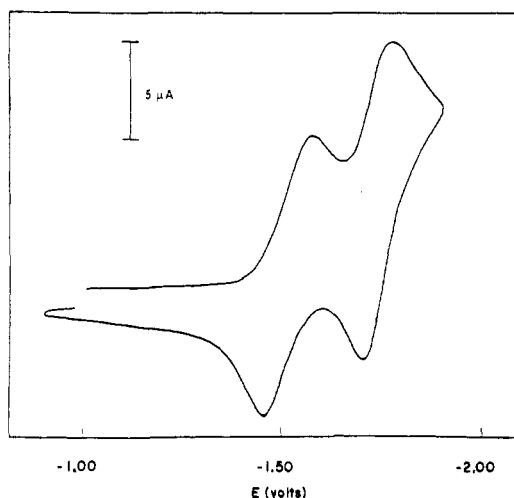


Figure 2. Cyclic voltammogram of  $1.018 \times 10^{-3}$  M  $\text{Ni}_2(\text{DBA})_2\text{-8py}$  in DMF with 0.10M TEAP at 1.000 V/s (HMDE).

peak potentials at  $-1.92$  and  $-2.10$  V. The similarity of these potentials to those of the ligand,  $\text{H}_4(\text{BAA})_2\text{en}$ , and  $\text{Ni}(\text{acac})_2\text{en}$  lead one to conclude that the wave at  $-1.92$  V is due to the ligand and the wave at  $-2.10$  V is  $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{I})$  reduction.

The cyclic voltammogram of the binuclear complex  $\text{Ni}_2(\text{BAA})_2\text{en}$  contains one quasi-reversible wave at  $E_{\text{pc}} = -1.53$  V in the range 0 to  $-2.3$  V. A typical cyclic voltammograms is shown in Figure 1. The irreversible prewave at about  $-1.4$  V is due to adsorption of a product reducing prior to the normal wave, as discussed by Wopschall and Shain.<sup>10</sup> At slow scan rates  $I_{\text{pc}}$  values, calculated by using eq 1<sup>11</sup> with  $\pi^{1/2}X(\alpha\tau) = 0.446$  for a one-

$$i_p = nFAO_0^*(\pi D_0\alpha)^{1/2}X(\alpha\tau) \quad (1)$$

electron process, are in good agreement with experimental values. At scan rates faster than  $0.500$  V/s, the cathodic peak splits into two components, simultaneously reducing the values of  $I_{\text{pc}}$  and  $I_{\text{pa}}$ . This behavior may be due to diffusion-controlled adsorption of reactants, for which the current function of the adsorption peak undergoes an increase with scan rate while the diffusion peak current function decreases. The function  $I_{\text{pc}}/v^{1/2}$  does decrease significantly at fast scan rates.

The cyclic voltammogram of the binuclear complex  $\text{Ni}_2(\text{DBA})_2$  in DMF, with a HMDE, exhibits two quasi-reversible waves in the 0 to  $-2.0$  V region. A typical cyclic voltammogram with cathodic peak potentials,  $E_{\text{pc}}$ , at  $-1.59$  and  $-1.77$  V is shown in Figure 2. The first wave exhibits  $I_{\text{pa}}/I_{\text{pc}}$  values of  $1.0 (\pm 0.1)$  in the scan rate range  $0.020$ – $5.00$  V/s and relatively constant  $I_{\text{pc}}/v^{1/2}$

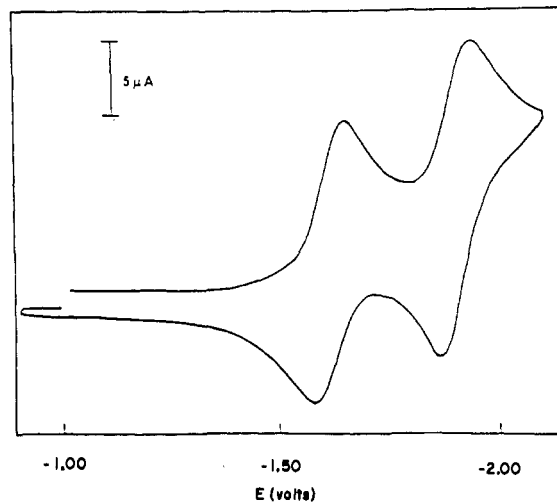


Figure 3. Cyclic voltammogram of  $0.970 \times 10^{-3}$  M  $\text{Ni}_2(\text{DBA})_2\text{-8py}$  in 4.8% (by volume) pyridine-DMF solution with 0.10 M TEAP at 1.000 V/s (HMDE).

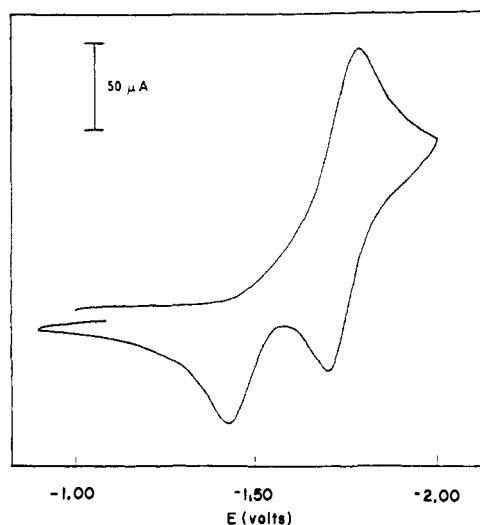


Figure 4. Cyclic voltammogram of  $1.018 \times 10^{-3}$  M  $\text{Ni}_2(\text{DBA})_2\text{-8py}$  in DMF with 0.10 M TEAP at 0.050 V/s (Pt disk).

values.  $\Delta E_p$  increases from 73 to 180 mV in this scan rate range while  $E_{\text{pc}} - E_{\text{pc}/2}$  increases from 65 to 108 mV. For the second wave,  $I_{\text{pa}}/I_{\text{pc}}$  is  $1.0 (\pm 0.1)$  for scan rates of  $0.020$ – $1.00$  V/s and increases to about 1.25 for  $2.00$ – $50.00$  V/s. The value of  $I_{\text{pc}}/v^{1/2}$  is reasonably constant throughout this range.  $\Delta E_p$  and  $E_{\text{pc}} - E_{\text{pc}/2}$  are quite constant at about 68 mV in the scan rate range  $0.020$ – $2.00$  V/s. At faster scans they increase slightly. The two waves are relatively unchanged as a function of scan rate up to about  $2.0$  V/s. At faster scans the first wave merges noticeably into the second. The peak-to-peak separation of the two cathodic waves is about 200 mV from  $0.020$  to  $0.500$  V/s and decreases significantly at faster scans. At  $5.00$  V/s the separation is 137 mV, resulting in wave distortion.

The number of electrons transferred in each wave shown in Figure 2 can be determined by the peak current values. Since both are reasonably reversible, eq 1 was used to compare experimental cathodic peak currents,  $I_{\text{pc}}$ , with calculated values. This calculation carried out for both waves (as a function of scan rate) using the current function  $\pi^{1/2}X(\alpha\tau) = 0.446$ , which is appropriate for a one-electron transfer, yielded excellent agreement with experimental observations. Thus, there seems no doubt that these are one-electron waves.

Addition of a good axial ligand such as pyridine (4.8% by volume) shifts the first wave of  $\text{Ni}_2(\text{DBA})_2$  cathodically by about 100 mV and the second by about 180 mV. the resultant cyclic voltammogram is presented in Figure 3. Moreover, on the basis of the values of  $\Delta E_p$ ,  $E_{\text{pc}} - E_{\text{pc}/2}$ , and  $I_{\text{pc}}/v^{1/2}$ , the addition of

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Table I

complex	reversibility	reducn potential, V vs. SSCE	
		-O <sub>2</sub> O <sub>2</sub> site	-N <sub>2</sub> O <sub>2</sub> site
Ni(acac) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	quasi	-1.70	
Ni(acac) <sub>2</sub> en	rev		-2.10
Ni(HBAA) <sub>2</sub> en	irrev		-1.92, <sup>a</sup> -2.10
Ni <sub>2</sub> (BAA) <sub>2</sub> en	quasi	1.58	not obsd
Ni <sub>2</sub> (DBA) <sub>2</sub>	quasi	-1.59, -1.77	

<sup>a</sup> Presumed to be ligand reduction since the free ligand has a reduction peak at -1.97 V.

pyridine increases the reversibility of both waves. The new values of  $E_{1/2}$  for the two waves are -1.63 and -1.92 V, respectively. The peak-to-peak separation under these conditions is about 300 mV.

A different type of behavior is observed for Ni<sub>2</sub>(DBA)<sub>2</sub> when the Pt disk electrode is used. Only one quasi-reversible one-electron wave is observed with  $E_{pc}$  at -1.8 V, this potential being related to the second reduction wave with the HMDE. On the other hand, another anodic wave occurs around -1.44 V, as shown in Figure 4. Values of  $I_{pc}$  calculated by using 1 and the one-electron current function are in good agreement with experimental values in the scan rate range 0.020–2.00 V/s. Thus, the reduction wave clearly corresponds to the transfer of one electron.

In each case, cyclic voltammograms were recorded in the presence of excess Na<sup>+</sup>, added as NaClO<sub>4</sub>, to investigate the effect of simple cations on the electron-transfer process. In no case, was any effect observed. There was no change in potentials or peak currents upon the addition of Na<sup>+</sup>.

Controlled-potential electrolysis (CPE) of Ni<sub>2</sub>(DBA)<sub>2</sub> in DMF with TEAP using a Hg pool electrode was carried out at -1.63 V (60 mV after the first reduction peak potential). The decay curve for the current–time plot does not reach zero current for long periods of time, resulting ultimately in the transfer of more than three electrons. CPE at -1.83 V (60 mV after the second reduction peak potential) resulted in the transfer of 6.3 electrons per molecular, indicating complete decomposition. In both cases it may be that the Ni(I) products catalyze an unknown ligand reaction.

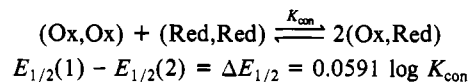
### Discussion

The mono- and binuclear Ni(II) complexes investigated constitute a series in which the Ni(II) environment is systematically varied from an oxygen donor atom environment (-O<sub>2</sub>O<sub>2</sub>) to one containing two diamine nitrogens and two keto oxygens (-N<sub>2</sub>O<sub>2</sub>). This allows reasonably straightforward assignment of the individual redox processes in the binuclear complexes. These results are summarized in Table I.

The reduction potentials for Ni(acac)<sub>2</sub> and Ni(acac)<sub>2</sub>en clearly establish what range of potentials to expect for Ni(II) in these environments. As a result, there seems little doubt that the values observed for Ni<sub>2</sub>(DBA)<sub>2</sub> and Ni<sub>2</sub>(BAA)<sub>2</sub>en correspond to the Ni(II) ⇌ Ni(I) redox process of Ni bound to four ketonate oxygens. It is curious that the redox for the -N<sub>2</sub>O<sub>2</sub> bound Ni(II) in Ni<sub>2</sub>(BAA)<sub>2</sub>en is not observed even though the cyclic voltammogram was recorded well beyond the expected value of -2.1 V. The charge on the first reduced species, [Ni<sub>2</sub>(BAA)<sub>2</sub>en]<sup>-</sup>, may shift the potential of the second Ni(II) to potentials more negative than -2.1 V due to repulsion between this intermediate and the electrode. At any rate, the reduction of the -N<sub>2</sub>O<sub>2</sub> bound Ni(II) is not observed more positive than -2.3 V.

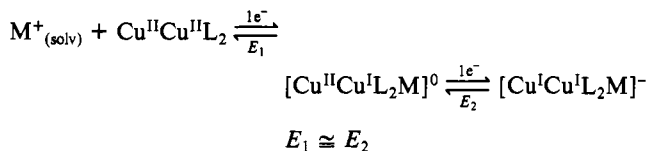
The symmetric binuclear complex Ni<sub>2</sub>(DBA)<sub>2</sub>, on the other hand, exhibits two nearly reversible CV waves in the region characteristic of ketonate oxygen coordination (Figure 2). Separation between these peaks is about 180 mV and varies somewhat with scan rate, ranging from 200 mV at slow scans to about 140 mV at 5 V/s. Addition of about 5% by volume of a strongly axially

coordinating ligand such as pyridine to the DMF solution improves the reversibility and increases the separation between the waves to about 300 mV (Figure 3). The separation between the waves is a measure of the stability of the mixed-valence species, [Ni<sup>II</sup>Ni<sup>I</sup>(DBA)<sub>2</sub>]<sup>-</sup>. This is generally represented as a conproportionality constant defined as follows:<sup>12</sup>



A peak separation of 300 mV yields a value of  $K_c = 1.2 \times 10^5$ , indicating a considerable thermodynamic stability for the mixed-valence intermediate. Unfortunately, CPE results do not indicate that the mixed-valence product can be easily studied, much less isolated. Electrolysis carried out at 60 mV beyond the first reduction peak resulted in the transfer of significantly more than 1.0 electron although the CV wave is clearly a one-electron-transfer wave; i.e., at least three electrons were transferred. Thus, there appears to be a competing process, perhaps catalytic, taking place on the long time scale of CPE that results in decomposition. This precludes isolation of the one-electron-reduction product under these conditions.

As stated above, one of the original purposes of this study was to compare and contrast the effect of added simple cations on the electrochemical properties of binuclear Cu(II) and binuclear Ni(II) complexes with the same or closely related ligands. The effect of cations such as Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, etc. on the binuclear Cu(II) complexes is profound in that they cause the sequential transfer of two electrons at very nearly the same potentials and shift the redox potentials by about +300 mV, thereby significantly increasing the stability of the Cu(I) reduction products.<sup>1-4</sup> Our interpretation of the results of several studies is that the cations bind strongly to the terminal oxygens of the reduced complexes.



The same results has been observed for the diamine Schiff-base derivative Cu<sub>2</sub>(BAA)<sub>2</sub>en<sup>3</sup> and even for the heterobinuclear complex NiCu(BAA)<sub>2</sub>en.<sup>2</sup> In principle, there is no apparent reason that analogous binuclear Ni(II) compounds should not behave similarly. However, the electrochemistry of the binuclear Ni(II) compounds shows no effect whatsoever of adding these simple cations to the cells. This is surprising since one would presume that the terminal oxygen electron pairs are as available in the Ni(II) complexes as in the Cu(II) complexes. The only obvious difference between the two is the strong requirement that N(II) has for axial ligands in this ketonate oxygen environment. It is possible that the axial ligands sterically preclude coordination of the partially solvated cations to the terminal oxygens. Whatever the reason, it is clear that simple cations have a very significant effect on the electrochemical behavior of the binuclear Cu(II) complexes and none on the binuclear Ni(II) analogues.

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**Registry No.** TEAP, 2567-83-1; Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, 14024-81-8; Ni(acac)<sub>2</sub>en, 36802-27-4; Ni(HBAA)<sub>2</sub>en, 55998-67-9; Ni<sub>2</sub>(BAA)<sub>2</sub>en(py)<sub>2</sub>, 102615-74-7; Ni<sub>2</sub>(DBA)<sub>2</sub>(py)<sub>4</sub>, 102615-75-8; [Ni(acac)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>-</sup>, 102615-76-9; [Ni<sub>2</sub>(DBA)<sub>2</sub>]<sup>-</sup>, 102615-77-0; [Ni(acac)<sub>2</sub>en]<sup>-</sup>, 77023-90-6; Pt, 7440-06-4; Hg, 7439-97-6.

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