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# Nickel(II) Complexes with Redox Noninnocent Octaazamacrocycles as Catalysts in Oxidation Reactions

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S Supporting Information

ABSTRACT: Nickel(II) complexes with 15-membered (1-5) and 14-membered (6) octaazamacrocyclic ligands derived from 1,2- and 1,3-diketones and S-methylisothiocarbohydrazide were prepared by template synthesis. The compounds were characterized by elemental analysis, electrospray ionization mass spectrometry, IR, UV-vis, <sup>1</sup>H NMR spectroscopies, and X-ray diffraction. The complexes contain a lowspin nickel(II) ion in a square-planar coordination environment. The electrochemical behavior of 1-6 was investigated in detail, and the electronic structure of 1e-oxidized and 1e-



reduced species was studied by electron paramagnetic resonance, UV-vis-near-IR spectroelectrochemistry, and density functional theory calculations indicating redox noninnocent behavior of the ligands. Compounds 1-6 were tested in the microwave-assisted solvent-free oxidation of cyclohexane by tert-butyl hydroperoxide to produce the industrially significant mixture of cyclohexanol and cyclohexanone (i.e., A/K oil). The results showed that the catalytic activity was affected by several factors, namely, reaction time and temperature or amount and type of catalyst. The best values for A/K oil yield (23%, turnover number of  $1.1 \times 10^2$ ) were obtained with compound 6 after 2 h of microwave irradiation at 100 °C.

# INTRODUCTION

Investigation of transition-metal complexes with redox noninnocent ligands has been an active area of research over the last three decades.<sup>1-9</sup> The main focus was initially on a detailed understanding of electronic structures of these compounds and their use in stoichiometric reactivity studies.<sup>10–13</sup> In particular, a cyclic tetrapeptide or macrolactam prepared by template reaction of nickel(II) salt with 2 mol equiv of dipeptide ester in methanol in the presence of NaOMe as base followed by addition of [PPN]Cl as countercation supplier (PPN = triphenyl-(triphenylphosphoranylidene)amino)phosphonium), and isolated as  $(PPN)_2[Ni(cyclo-Gly-\beta-Ala)_2-4H^+]$  (I in Chart 1),<sup>14</sup> was found to react in acetonitrile (ACN) in air with formation of deep red solution.  $\alpha$ -Hydroxylation of the glycine segment occurred to give  $(PPN)_2[Ni(cyclo-\alpha-OH-Gly-\beta-Ala)_2-4H^+]$  (II in Chart 1) as confirmed by X-ray crystallography.<sup>15</sup> The formation of nickel(III)-oxyl species as intermediates in stoichiometric transformations was suggested via generation

Chart 1. Line Drawing of the Complex Anions I and II in  $(PPN)_2[Ni(cyclo-Gly-\beta-Ala)_2-4H^+]$  and  $(PPN)_2[Ni(cyclo-\alpha-\alpha-\alpha)_2-4H^+]$ OH-Gly- $\beta$ -Ala)<sub>2</sub>-4H<sup>+</sup>], Respectively



of nickel(III) and a glycine radical in the first steps of the reaction.

Nowadays, the use of first-row transition-metal complexes with noninnocent ligands in catalytic reactions is rising. Catalytic functionalization of C-H bonds and activation of

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small molecules are well-documented in the literature.<sup>16–19</sup> Redox-active ligands can participate in the catalytic cycle by accepting or donating electrons and modifying the Lewis acidity of the metal and in the formation/breaking of substrate covalent bond electron transfer events upon bond activation serving as an electron reservoir.<sup>20</sup>

The rational design of efficient oxidation catalysts requires an understanding of the structure and spectroscopic properties, as well as the reactivity of the key reactive species. Nickel(II) complexes have attracted the interest of researchers in selective hydroxylation of saturated hydrocarbons. In particular, Ni<sup>II</sup>(TPA) (TPA = tris(2-pyridylmethyl)amine, Chart 2) was

Chart 2. Line Drawings of TPA and TMG<sub>3</sub>tren



found effective for cyclohexane hydroxylation with *m*-chloroperbenzoic acid (*m*-CPBA). A possible contribution of the intermediate Ni<sup>III</sup>-oxido species was suggested.<sup>21,22</sup> The formation of Ni<sup>III</sup>-oxygen intermediates upon the reaction of  $[Ni^{II}(TMG_3tren)]^{2+}$  ( $TMG_3tren = tris[2-(N-tetramethylguanidyl)ethyl]amine, Chart 2$ ) with *m*-CPBA at low temperature was evidenced by electron paramagnetic resonance (EPR) and UV-vis spectroscopic measurements.<sup>23</sup>

Tetraazamacrocyclic nickel(II) complexes with highly basic ligand structures containing carboxamidate groups (e.g., III in Chart 3) have been discovered to oxidize the cyclohexane to cyclohexanone and cyclohexanol via high-valent Ni<sup>III</sup>–oxyl radical intermediate.<sup>24,25</sup>

#### Chart 3. Nickel(II) Bis(amidate) Complex III



Nickel(II) complexes with S-substituted isothiosemicarbazides  $(H_2NNC(SR)NH_2)$  and isothiosemicarbazones  $(R_1R_2C=NNC(SR)NH_2)$  are known for their redox noninnocent properties.<sup>26</sup> The isothiocarbohydrazides (NH<sub>2</sub>NC- $(SR)NHNH_2$ ) and isothiocarbohydrazones  $(R_1R_2C=NNC-$ (SR)NHNH<sub>2</sub>) are closely related derivatives and might also exhibit redox noninnocent behavior.<sup>27</sup> Moreover, vanadium-(V) complexes with Schiff bases of carbohydrazone  $(H_2NNHCONHNH_2)$  were found to be efficient in peroxidative oxidation of cyclohexane in cyclohexanol and cyclohexanone under solvent-free low-power microwave (MW) irradiation. The key role of the carbohydrazone ligand, which might undergo reduction to an active form of the catalyst, was suggested from density functional theory (DFT) calculations.<sup>28</sup> Herewith we report on the template synthesis of nickel(II) complexes with 15- and 14-membered octaazamacrocyclic ligands 1-6 (Chart 4), their structure, and spectroscopic properties of 1e-oxidized and 1e-reduced species.

# Chart 4. Complexes Reported in This Work<sup>a</sup>



<sup>*a*</sup>Underlined numbers indicate complexes studied by X-ray crystallography.

The ability of these complexes to catalyze the microwaveassisted solvent-free oxidation of cyclohexane by *tert*-butyl hydroperoxide (TBHP) to the industrially significant mixture of cyclohexanol and cyclohexanone (i.e., A/K oil) was tested, and the results are discussed.

#### EXPERIMENTAL SECTION

New, more convenient synthetic protocols providing higher yields are described below for previously communicated compounds **2**, **3**, and **6**.<sup>29,30</sup> Diphenylglyoxal-bis(*S*-methylisothiocarbohydrazonato)nickel-(II) was synthesized by following a published protocol.<sup>30</sup> 1-(4-Pyridinyl)butane-1,3-dione was obtained as described in the literature.<sup>31</sup>

Synthesis of Complexes. Complex 1. To a hot solution of NiCl<sub>2</sub>·6H<sub>2</sub>O (3.60 g, 15.1 mmol), S-methylisothiocarbohydrazidium iodide (7.5 g, 30.2 mmol) and pyridine (5.0 g, 63.0 mmol) in water (200 mL) was added dropwise over 30 min a solution of freshly distilled diacetyl (1.3 g, 15.1 mmol) in water (30 mL). The mixture was heated at 100 °C for 10 min, and after it cooled, the precipitate formed was filtered off, washed thoroughly with water, and dried in vacuo. The solution of this raw product in dimethylformamide (DMF; 80 mL) was added dropwise over 80 min to the boiling pentan-2,4dione (50 mL). The mixture was refluxed for 1 h, and after it cooled, the precipitate formed was filtered off, washed with DMF, until the washing solution became almost colorless, and then with methanol, and dried in vacuo. Yield: 2.84 g (46%) of dark red crystals. Anal. Calcd for  $C_{13}H_{20}NiN_8S_2$  ( $M_r = 411.18$ ): C, 37.97; H, 4.90; N, 27.25; S, 15.60%. Found, %: C, 37.80; H, 4.72; N, 26.88; S, 15.21. IR (most characteristic bands, cm<sup>-1</sup>): 1623m, 1512s, 1458s, 1414s, 1295s, 1265s, 1159s, 1008s. <sup>1</sup>H NMR CDCl<sub>3</sub>, δ, ppm: 2.10 (s, 3H), 2.30 (s, 3H), 2.44 (s, 6H), 2.51 (s, 3H), 2.60 (s, 3H), 3.60 (s, 2H). ESI MS (positive ion mode for <sup>58</sup>Ni): m/z 411 [M + H]<sup>+</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{\rm max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 502 (5250), 463 (5073), 390 (3177), 323(11730).

Complex 2. Diphenylglyoxal-bis (S-methylis othiocarbohydrazonato)nickel(II) (1.0 g, 2.1 mmol) and pentan-2,4dione (4 mL, 39 mmol) were stirred at 130  $^{\circ}$ C under argon for 8 h. The volatile components of the reaction mixture were removed under reduced pressure. The residue was washed with ethanol until the washing solution become almost colorless and purified by column

Table 1. Crystal Data and Details of Data Conection for 5-5 and 0.2D	Table	e 1.	Crv	stal	Data	and	Details	of Data	Collection	for	3 - 5	and	6·2DM
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compound	3	4	5	6·2DMF
empirical formula	C28H26N8NiS2	$C_{33}H_{28}N_8NiS_2$	C27H25N9NiS2	$C_{38}H_{40}N_{10}NiO_2S_2$
fw	597.40	659.46	598.39	791.64
space group	$P2_1/n$	Pbcn	P21/c	$P2_1/c$
a [Å]	14.5257(14)	16.396(3)	15.2262(6)	11.0723(2)
b [Å]	9.1384(5)	22.138(4)	11.3590(5)	9.3423(2)
c [Å]	21.4350(18)	16.751(3)	16.4526(8)	18.1275(4)
$\alpha$ [deg]				
$\beta$ [deg]	107.792(3)		112.421(2)	92.317(2)
γ [deg]				
$V [Å^3]$	2709.2(4)	6080(2)	2630.4(2)	1873.59(7)
Ζ	4	8	4	2
λ [Å]	0.710 73	0.700 00	0.710 73	1.541 86
$\rho_{\rm calcd}  [{ m g \ cm^{-3}}]$	1.465	1.441	1.511	1.403
crystal size [mm]	$0.12 \times 0.09 \times 0.03$	$0.03 \times 0.005 \times 0.005$	$0.13 \times 0.06 \times 0.03$	$0.12 \times 0.08 \times 0.03$
T[K]	100(2)	100(2)	100(2)	100(2)
$\mu \text{ [mm}^{-1}\text{]}$	0.905	0.777	0.933	2.186
$R_1^{a}$	0.0600	0.0553	0.0450	0.0329
$wR_2^b$	0.1106	0.1597	0.0934	0.0804
GOF <sup>c</sup>	0.980	1.019	0.996	0.934

 ${}^{a}R_{1} = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|. {}^{b}wR_{2} = \{\sum [w(F_{0}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{0}^{2})^{2}]\}^{1/2}. {}^{c}GOF = \{\sum [w(F_{0}^{2} - F_{c}^{2})^{2}] / (n-p)\}^{1/2}, where n is the number of reflections, and p is the total number of parameters refined.$ 

chromatography on silica using chloroform as eluent. The second red fraction collected was evaporated; the product was washed with ethanol and dried in vacuo. Yield: 0.85 g (75%) of dark red crystals. Anal. Calcd for C<sub>23</sub>H<sub>24</sub>NiN<sub>8</sub>S<sub>2</sub> ( $M_r$  = 536.32): C, 51.60; H, 4.52; N, 20.93; S, 11.98%. Found: C, 51.74; H, 4.40; N, 20.63; S, 11.48%. IR (most characteristic bands, cm<sup>-1</sup>): 1538m, 1505s, 1493s, 1441s, 1398s, 1239vs, 1244s, 1247s, 1205vs, 944vs, 914s, 694vs. <sup>1</sup>H NMR CDCl<sub>3</sub>,  $\delta$ , ppm: 2.13 (s, 3H), 2.16 (s, 3H), 2.45 (s, 3H), 2.50 (s, 3H), 3.72 (s, 2H), 7.03–7.12 (m, 6H), 7.14–7.19 (m, 4H). ESI MS (positive ion mode for <sup>58</sup>Ni): m/z 535 [M + H]<sup>+</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 519 (11 200), 468sh, 402 (8207), 340 (19 615).

Complex 3. Diphenylglyoxal-bis (S-methylisothiocarbohydrazonato)nickel(II) (1.0 g, 2.1 mmol) and excess of benzoylacetone (1.7 g, 10.4 mmol) were heated at 140 °C under argon for 6 h. Then the unreacted benzoylacetone was removed under reduced pressure. The residue was purified on silica by using chloroform as eluent. The main red fraction collected was evaporated, and the product was washed with ethanol and dried in vacuo. Yield: 0.92 g (66%) of red crystals. Anal. Calcd for  $C_{28}H_{26}NiN_8S_2$  ( $M_r$  = 597.39): C, 56.30; H, 4.39; N, 18.76; S, 10.74%. Found, %: C, 55.93; H, 4.33; N, 18.32; S, 10.44. IR (most characteristic bands, cm<sup>-1</sup>): 1504s, 1458s, 1440s, 1399s, 1324s, 1292vs, 1247s, 1208vs, 949s, 926s, 699vs. <sup>1</sup>H NMR CDCl<sub>3</sub>,  $\delta$ , ppm: 1.94 (s, 3H), 2.14 (s, 3H), 2.15 (s, 3H), 4.05 (s, 2H), 6.97–7.57 (m, 15). ESI MS (positive ion mode for <sup>58</sup>Ni): m/z 597 [M + H]<sup>+</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max}$  nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 534 (10 949), 469sh, 409 (12 623), 362 (25 017).

*Complex* **4**. A mixture of diphenylglyoxal-bis(*S*-methylisothiocarbohydrazonato)nickel(II) (1.0 g, 2.1 mmol) and dibenzoylmethane (1.5 g, 6.7 mmol) was heated at 130 °C under argon for 6 h. After it cooled, the residue was stirred in hot EtOH (10 mL) for 20 min, filtered off, washed with ethanol and dried, then dissolved in CHCl<sub>3</sub>, and purified by column chromatography (SiO<sub>2</sub>, eluent CHCl<sub>3</sub>). The second red fraction was collected, and the volatiles were evaporated; the product was washed with ethanol and dried in vacuo. Yield: 0.92 g (66%) of red crystals. Anal. Calcd for  $C_{33}H_{28}NiN_8S_2$  ( $M_r = 659.45$ ): C, 60.10; H, 4.28; N, 16.99; S, 9.73%. Found, %: C, 59.85; H, 4.22; N, 16.88; S, 9.81. IR (most characteristic bands, cm<sup>-1</sup>): 1494s, 1461s, 1441s, 1396s, 1295s, 1209vs, 934s, 691vs. <sup>1</sup>H NMR CDCl<sub>3</sub>,  $\delta$ , ppm: 2.19 (s, 3H), 2.21 (s, 3H), 4.55 (s, 2H), 7.07(s, 6H), 7.11–7.23(m, 6H), 7.44–7.49(m, 6H), 7.56–7.59(m, 2H). ESI MS (positive ion mode for <sup>58</sup>Ni): *m/z*  659 [M + H]<sup>+</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max}$ , nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 535 (16 734), 473sh, 410sh, 365(42 594), 335 (43 436).

Complex 5. A mixture of diphenylglyoxal-bis(S-methylisothiocarbohydrazonato)nickel(II) (0.2 g, 0.42 mmol) and 1-(4-pyridinyl)butane-1,3-dione (0.8 g, 4.9 mmol) was heated at 130 °C under argon for 8 h. After it cooled, the separated precipitate was filtered off and washed with diethyl ether. The raw product was purified on silica by using chloroform as eluent. The third red fraction was collected, and the solvent was removed under reduced pressure. The product was washed with ethanol (3 mL) and dried in vacuo. Yield: 0.11 g (44%) of red crystals. Anal. Calcd for  $C_{27}H_{25}NiN_9S_2$  ( $M_r = 598.37$ ): C, 54.20; H, 4.21; N, 21.07; S, 10.72%. Found, %: C, 53.81; H, 4.13; N, 20.90; S, 10.41. IR (most characteristic bands, cm<sup>-1</sup>): 1589m, 1534s, 1487s, 1407vs, 1324vs, 1251s, 1208vs, 948vs, 701vs. <sup>1</sup>H NMR CDCl<sub>3</sub>, δ: 2.01 (s, 3H), 2.13 (s, 3H), 2.19 (s, 3H), 4.06 (s, 2H), 7.08, 7.18 (10H), 7.53 (s, 2H), 8.78 (s, 2H). ESI MS (positive ion mode for <sup>58</sup>Ni): m/z 620 [M + Na]<sup>+</sup>, (negative ion mode): m/z 596 [M–H]<sup>-</sup>. UV-vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 542 (11042), 467sh, 405sh, 365 (26792).

*Complex* **6.** A mixture of diphenylglyoxal-bis(*S*-methylisothiocarbohydrazonato)nickel(II) (1.0 g, 2.1 mmol) and benzil (2.0 g, 9.5 mmol) was heated at 140 °C under argon for 6 h. The residue was washed thoroughly with acetone, DMF, and acetone, until almost colorless washing solution, and dried in vacuo. Yield: 0.95 g (69%) of dark green powder. Anal. Calcd for  $C_{32}H_{26}NiN_8S_2$  ( $M_r = 645.43$ ): C, 59.55; H, 4.06; N, 17.36; S, 9.94%. Found, %: C, 59.52; H, 4.04; N, 17.23; S, 10.25. IR (most characteristic bands, cm<sup>-1</sup>): 1486s, 1383s, 1302s, 1250s, 1208vs, 1093s, 949vs, 709vs, 691vs. <sup>1</sup>H NMR CDCl<sub>3</sub>,  $\delta$ , ppm: 2,16 (s, 3H), 7.00–7.20 (20H). ESI MS (positive ion mode for <sup>58</sup>Ni): m/z 645 [M + H]<sup>+</sup>. UV–vis (CH<sub>2</sub>Cl<sub>2</sub>),  $\lambda_{max}$ , nm ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 608 (8402), 562 (5882), 523sh, 448 (10 372), 429 (10 299), 400 (12 954), 377sh, 344 (18 238).

**Crystallographic Structure Determination.** X-ray diffraction quality single crystals of **3–5** were grown by slow evaporation of chloroform–ethanolic solutions. Crystals of **6·2DMF** were obtained by recrystallization of **6** from DMF. The measurements were performed on a Bruker X8 APEXII CCD (**3** and **5**) and STOE (**6· 2DMF**) diffractometers. Single crystals were positioned at 35, 35, and 40 mm from the detector, and 512, 1645, and 7610 frames were measured, each for 20, 40, and 2/12 s over 0.5, 0.5, and 0.25° scan width for **3**, **5**, and **6·2DMF**, respectively. The data were processed using SAINT and STOE X-RED software.<sup>32</sup> Compound **4** was measured at the XRD2 structural biology beamline, Elettra synchrotron. The beamline is equipped with an Arinax MD2S diffractometer and a Pilatus 6 M area detector, and monochromated X-rays are provided by a super conducting wiggler followed by a dual crystal monochromator. Frame integration was performed using the XDS package.<sup>33</sup> Up to 12 crystals of 4 were tested. The sample generally showed poor crystallinity, and, while most data sets could be processed to reasonable  $R_{int}$  values, the structure could not be refined to an R factor below 10%. Twin analysis was inconsistent, and it was concluded that the measured crystals were aggregates. At this point a small crystal of 5  $\times$  5  $\times$  30  $\mu$ m was selected. The crystal was weakly diffracting, and the resolution of the collected X-ray data has been estimated to be 1.1 Å. Nevertheless the structure could be solved, and electron density maps allowed for the determination of the atomic connectivity. Crystal data, data collection parameters, and structure refinement details are given in Table 1. The structures were solved by direct methods and refined by full-matrix least-squares techniques. Non-H atoms were refined with anisotropic displacement parameters. H atoms were inserted in calculated positions and refined with a riding model. The following computer programs and hardware were used: structure solution, SHELXS-2014 and refinement, SHELXL-2014;<sup>34</sup> molecular diagrams, ORTEP;<sup>35</sup> computer, Intel CoreDuo. See Supporting Information for more information about CCDC 1921435 (3), 1921438 (4), 1921436 (5), and 1921437 (6·2DMF).

Electrochemistry and Spectroelectrochemistry. The cyclic voltammetric studies were performed in a homemade miniature electrochemical cell using platinum-disk working electrode (from Ionode, Australia), a platinum wire as the counter electrode, and silver wire as pseudoreference electrode. Ferrocene served as the internal potential standard, and the potentials were determined versus ferricenium/ferrocene couple. A Heka PG310USB (Lambrecht, Germany) potentiostat with a PotMaster 2.73 software package was used in cyclic voltammetric and spectroelectrochemical studies. In situ spectroelectrochemical measurements were performed on a spectrometer Avantes, model AvaSpec-2048 × 14-USB2, under an argon atmosphere in a spectroelectrochemical cell kit (AKSTCKIT3) with the Pt-microstructured honeycomb working electrode, purchased from Pine Research Instrumentation. Halogen and deuterium lamps were used as light sources (Avantes, model AvaLight-DH-S-BAL). The cell was positioned in the CUV-UV Cuvette Holder (Ocean Optics) connected to the diode-array UV-vis-NIR (NIR = nearinfrared) spectrometer by optical fibers. UV-vis-NIR spectra were processed using the AvaSoft 7.7 software package. EPR spectra were recorded with the EMXplus X-band EPR spectrometer (Bruker, Germany).

Computational Details. Standard B3LYP/6-311G\*<sup>36-42</sup> geometry optimization in various spin states was performed using the Gaussian09<sup>43</sup> program package. For open-shell systems, the unrestricted DFT formalism was used; that is, B3LYP implies UB3LYP. Solvent effects in dichloromethane, acetonitrile, and dimethylformamide were approximated by the integral equation formalism polarizable continuum model (IEFPCM)<sup>44,45</sup> as implemented in Gaussian09. The stability of the optimized structures was confirmed by vibrational analysis (no imaginary vibrations). The g tensors<sup>46,47</sup> were evaluated using the ORCA 3.0.3 software package. Calculation in ORCA accounted for the COSMO<sup>49</sup> solvent model of dichloromethane using BLYP and B3LYP functionals. Hyperfine interaction constants were approximated by the Fermi contact interaction as given in the Gaussian09 output files. The IQmol package<sup>50</sup> was used for the visualization of the molecular orbitals and spin densities using the Gaussian09 fchk. The atomic d-populations on the central nickel atom and the atomic orbital populations of localized orbitals were obtained via the Mulliken population analysis (MPA) as implemented in Gaussian09 and ORCA packages. Atomic charges and bond characteristics were obtained from the Quantum Theory of Atoms in Molecules (QTAIM)<sup>51</sup> using the AIMAll package.52

**Catalytic Studies.** The catalytic tests for cyclohexane oxidation were performed in a microwave Anton Paar Monowave 300 (25 W), using a G10 MW borosilicate glass tube. To the G10 reaction tube,

1–20  $\mu$ mol of 1–6, 2.50 mmol of cyclohexane, and 5.00 mmol of 70% aqueous (aq) *tert*-butyl hydroperoxide (TBHP) were added. The tube was placed in the MW reactor, and the system was stirred (800 rpm) and irradiated (10 W) for 0.5–3 h at 60 to 100 °C. After the reaction, the mixture was cooled to room temperature, and a sample was analyzed by gas chromatography (GC). For the MW assays in the presence of a radical trap, NHPh<sub>2</sub> in a stoichiometric amount relative to TBHP was further added to the reaction mixture. For the reactions performed under conventional heating, the reagents (as above) were introduced into a round-bottomed flask (25 mL) adapted to a reflux condenser, immersed in an oil bath (60–100 °C).

A FISONS Instruments GC 8000 gas chromatograph equipped with a DB-624 (J&W) capillary column (with flame ionization detector (FID)) and Jasco-Borwin v.1.50 software were used for the GC measurements. Helium was the carrier gas. The temperature of the injection was 240 °C. The initial temperature (120 °C) of the column was maintained for 1 min, then raised 10 °C/min to 200 °C, and held at this temperature for 1 min. The attribution of the GC peaks was accomplished by comparison with the chromatograms of pure cyclohexane, cyclohexanol, and cyclohexanone. Quantification by the internal standard method was performed on the basis of calibration curves constructed with known concentrations of samples of cyclohexane, cyclohexanol, cyclohexanone, and nitromethane. Subsequently, following a method developed by Shul'pin,<sup>53-59</sup> an excess of triphenylphosphine was added to the sample, and the resulting mixture was analyzed again to estimate the amount of the cyclohexyl hydroperoxide primary product formed. Gas chromatography-mass spectrometry (GC-MS) analyses were performed using a PerkinElmer Clarus 600 C instrument (using helium as the carrier gas). The ionization voltage was 70 eV. GC experiments were conducted in the temperature-programming mode, using an SGE BPX5 column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu$ m). The products were identified by comparison of their retention times with pure reference compounds, as well as of their mass spectra to fragmentation patterns obtained from the National Institute of Standards and Technology (NIST) spectral library of the software of the mass spectrometer.

Blank experiments, in the absence of 1-6, were performed under the optimized reaction conditions, and no cyclohexane conversion was detected. Experiments with NiCl<sub>2</sub>·6H<sub>2</sub>O were run using the optimized reaction conditions found for 1-6. The obtained A/K oil yield under such conditions was 0.8%.

#### RESULTS AND DISCUSSION

Synthesis of Complexes. Complexes 1-6 were prepared in two steps as shown in Scheme 1. First, the reaction of

Scheme 1. Synthesis of 1-6



diacetyl and/or diphenylglyoxal with 2 mol equiv of Smethylisothiocarbohydrazidium iodide in water or ethanol in the presence of pyridine or ammonia as a base afforded the nickel(II) complexes with open-chain tetradentate ligands (species A in Scheme 1).

Then the reactions of the latter with glyoxal, acetylacetone (Hacac), benzoylacetone (Hbzac), dibenzoylmethane, 1-(4-pyridinyl)-butane-1,3-dione, and diphenylglyoxal afforded the products 1-6, respectively, in different yields (11 to 69%). The formation of macrocyclic complexes 1-6 was confirmed by the strong peaks in positive ion ESI mass spectra, which



**Figure 1.** (a) ORTEP plot of **3** with atom-labeling scheme and thermal ellipsoids drawn at 50% probability level. Selected bond distances (Å), bond angles, and dihedral angles (deg): Ni–N2 = 1.846(4), Ni–N5 = 1.872(4), Ni–N10 = 1.897(4), and Ni–N13 = 1.809(4); N2–Ni–N5 = 82.98(16), N5–Ni–N10 = 102.21(17), N10–Ni–N13 = 82.62(16), N2–Ni–N13 = 92.18(17); N6–C7–C8–C9 = 83.2(6); (b) ORTEP plot of **5** with atom-labeling scheme and thermal ellipsoids drawn at 50% probability level. Selected bond distances (Å), bond angles, and dihedral angles (deg): Ni–N2 = 1.8382(19), Ni–N5 = 1.861(2), Ni–N10 = 1.8812(19), and Ni–N13 = 1.806(2); N2–Ni–N5 = 83.83(8), N5–Ni–N10 = 102.24(8), N10–Ni–N13 = 82.27(8), N2–Ni–N13 = 92.37(9); N6–C7–C8–C9 = -81.3(3).

could be attributed to  $[M + H]^+$  or  $[M + Na]^+$  ions. <sup>1</sup>H NMR spectra were in accordance with the  $C_1$  molecular symmetry for 1–5. Notice that the spectrum of 6 is in agreement with the  $C_{2h}$  molecular symmetry suggested for this compound, at least for some particular conformations. The thiomethyl group protons were observed in the spectrum at 2.16 ppm.

The isolation of intermediates **A** was possible because of the steric nonequivalence of end amine groups in *S*-methyliso-thiocarbohydrazidium iodide<sup>60</sup> (Figure S1). Independent of the conformation adopted, the thiomethyl group creates steric hindrance for one of the two end NH<sub>2</sub> groups. Note that only one geometric isomer from the two possibilities was isolated for **3** and **5**. The structures of the isomers shown below are favored, since one of the SCH<sub>3</sub> groups exerts steric hindrance at the end noncoordinated NH<sub>2</sub> group, whereas the second is far away from the coordinated NH<sub>2</sub> group and is not able to affect the availability of this for further condensation reaction. Distinct steric requirements for R<sub>3</sub> and R<sub>4</sub> in 1,3-diketone



**Figure 2.** (a) ORTEP plot of 4 with atom-labeling scheme and thermal ellipsoids drawn at 50% probability level. Selected bond distances (Å), bond angles, and dihedral angles (deg): Ni–N2 = 1.851(7), Ni–N5 = 1.861(8), Ni–N10 = 1.882(7), and Ni–N13 = 1.798(8); N2–Ni–N5 = 83.7(4), N5–Ni–N10 = 102.0(4), N10–Ni–N13 = 82.4(4), N2–Ni–N13 = 91.7(4), and N6–C7–C8–C9 = -79.7(11). (b) ORTEP plot of 6 with atom-labeling scheme and thermal ellipsoids drawn at 50% probability level. Selected bond distances (Å) and bond angles (deg): Ni–N2 = 1.8183(15), Ni–N5 = 1.7928(15); N2–Ni–N5 = 84.82(7), N5<sup>i</sup>–Ni–N2 = 95.18(7). (i) –x + 1, –y + 1, –z + 1.

result in the formation of predominantly one geometric isomer from the two possible (vide infra).

X-ray Crystallography. The results of X-ray diffraction studies of 3-5 and 6 are shown in Figures 1 and 2, respectively, with selected bond distances and bond angles quoted in the legends. All complexes studied, except 4, crystallized in monoclinic space groups, 3 crystallized in  $P2_1/n_1$ and 5 and 6 crystallized in  $P2_1/c$ . Complex 4 crystallized in the orthorhombic Pbcn space group. The crystals of complexes 3-5 do not contain cocrystallized solvent, whereas 6 contains two cocrystallized DMF molecules per molecule of 6. Complexes 3-5 contain 15-membered octaazaamacrocyclic ligands, while 6 has a 14-membered octaazamacrocyclic ligand. The 15membered ligands are not planar due to the presence of one sp<sup>3</sup>-hybridized methylene group in the macrocycle, which interrupts the conjugation, while the 14-membered macrocycle in 6 is essentially flat. The nickel(II) in 3-5 and 6 adopts a square-planar N<sub>4</sub> coordination geometry due to a strong ligand field of the tetradentate ligands. The bond lengths Ni-N2, Ni-N5, Ni-N10, and Ni-N13 in 3 and 5 are very similar.



Figure 3. Cyclic voltammograms for complexes (a) 1, (b) 2, (c) 4, and (d) 6 in DCM/ $nBu_4NPF_6$  solutions (Pt-disc working electrode, scan rate 100 mV s<sup>-1</sup>).

Table 2. Electrochemical Data Versus  $Fc^+/Fc$  for 1–6 in  $DCM/nBu_4NPF_6$  Solutions<sup>*a*</sup>

complex	$E_{1/2}^{\rm red}$	$E_{1/2}^{\text{ox1}}$	$E_{1/2}^{\text{ox2}}$
1	-2.08	0.53	0.82
2	-1.90	0.58	0.96
3	-1.80	0.57	0.95
4	-1.62	0.57	0.87
5	-1.75	0.69	1.06
6	-1.38	0.79	1.03
	-2.01		

<sup>*a*</sup>Electrochemical data in volts. Pt working electrode, scan rate 100 mV s<sup>-1</sup>.

Three kinds of chelate cycles, namely, five-, six-, and sevenmembered, are present in 3-5, and only two, five- and sixmembered, are in 6. A 10° increase of the bite angle is of note when passing from five- to six- and to seven-membered chelate rings in 3-5. The same incremental increase of the bite angle is observed in 6 when going from five- to six-membered chelate rings. A portion of the crystal structure of 3 showing the formation of ribbons via weak intermolecular contacts C-H··· S of 3.74 Å is shown in Figure S2, while a fragment of onedimensional (1D) chain in the crystal structure of 4 is shown in Figure S3. Figure S4 reveals the presence of dimers in the crystal structure of 5 associated via weak intermolecular contacts Ni···S of 3.42 Å, while Figure S5 shows a 1D arrangement of macrocyclic complexes and of cocrystallized DMF molecules in the crystal of 6·2DMF.

Electrochemistry and Spectroelectrochemistry. Two reversible oxidation waves and one or two reduction steps were observed for all investigated Ni<sup>II</sup>L complexes 1-6 in the potential window available, as shown in cyclic voltammograms in Figure 3 for 1, 2, 4, and 6 in dichloromethane (DCM) solutions. Very similar results were obtained in ACN solutions of the complexes (not shown), although the solubility was markedly lower. The UV–vis spectra of initial solutions of 1-6 are shown in Figure S6.

Electrochemical data for 1-6 derived from the cyclic voltammetry in DCM/*n*Bu<sub>4</sub>NPF<sub>6</sub> solutions using Pt working electrode and a scan rate of 100 mV s<sup>-1</sup> are summarized in Table 2.

In contrast to the cathodic reduction, the first anodic oxidation step of 1-5 is much less dependent on the macrocycle substitution (half-wave oxidation potential is in the range from +0.53 to +0.69 V vs Fc<sup>+</sup>/Fc) suggesting a partial contribution of the Ni<sup>II</sup> ion to the redox behavior. Only for **6**, a higher oxidation potential at +0.79 V versus Fc<sup>+</sup>/Fc was observed. The second oxidation peak is, for all complexes, more dependent on the substitution pattern indicating a ligand-centered second electron transfer. The oxidation of **1** shows electrochemically irreversible characteristics at 100 mV s<sup>-1</sup>, but the cyclic voltammograms become more reversible at



Figure 4. Cyclic voltammograms for 1 in the region of the first oxidation peak (a) and going to the second oxidation wave (b) at different scan rates in  $DCM/nBu_4NPF_6$  (Pt-disc working electrode).

higher scan rates (1000 mV s<sup>-1</sup>), as shown in Figure 4, indicating moderate stability of the generated cation 1<sup>+</sup>.

ACN was found to be the best solvent for spectroelectrochemistry of complexes 1-6 in the anodic part. Upon anodic oxidation of 2 in ACN/*n*Bu<sub>4</sub>NPF<sub>6</sub>, a reversible redox couple was observed in the corresponding cyclic voltammogram even at a low scan rate of 10 mV s<sup>-1</sup>. The oxidation of 2 was accompanied by a simultaneous evolution of new absorption band at 640 nm via isosbestic points at 565 and 475 nm (Figure 5a).

Simultaneously, a single-line X-band EPR spectrum was observed with  $g_{iso}$  value of 2.0995 and a line width  $\Delta B_{pp} = 4.3$ mT at room temperature (Figure S6a). The shift of the  $g_{iso}$ from the free electron value of 2.0023 indicates that the oneelectron oxidation of 2 generates a ligand-centered radical with a pronounced delocalization of the unpaired spin onto the nickel ion.<sup>61-64</sup> A spectroelectrochemical experiment coupled with X-band EPR measurement at 110 K allowed the EPR characterization of electrochemically generated  $[2]^+$  in frozen solution (Figure 5b). The rhombic EPR signal with a rather large g-tensor anisotropy ( $g_1 = 2.172$ ,  $g_2 = 2.125$ , and  $g_3 =$ 1.979) suggests that, while  $[2]^+$  cannot be explicitly described as a nickel(III) species, the contribution of the central nickel ion is rather significant.<sup>64</sup> Similar redox behavior and EPR spectra were measured also for other 1e-oxidized nickel(II) complexes as shown for 5 in Figure S7b.



**Figure 5.** In situ UV–vis–NIR and ex situ EPR spectroelectrochemistry of **2** in ACN/*n*Bu<sub>4</sub>NPF<sub>6</sub> under an argon atmosphere: (a) UV– vis–NIR spectra measured in the region of the first anodic peak upon forward scan with the corresponding cyclic voltammogram (see inset, scan rate  $\nu = 10$  mV s<sup>-1</sup>); (b) representative EPR spectrum (black line) observed for [**2**]<sup>+</sup> in frozen ACN solution at 110 K and its simulation (red line,  $g_1 = 2.169$ ,  $g_2 = 2.126$ ,  $g_3 = 1.986$ ).

In the cathodic part, the most negative half-wave reduction potential  $(E_{1/2}^{\text{red}})$  was observed for 1, featuring only methyl substituents, at -2.08 V versus Fc<sup>+</sup>/Fc, while less negative reduction potential at  $E_{1/2} = -1.75$  V versus Fc<sup>+</sup>/Fc was observed for 4 with four phenyl substituents instead of methyl groups. Even less negative reduction potential was found for 5 at -1.62 V versus Fc<sup>+</sup>/Fc, where pyridyl was present instead of one phenyl group. Generally, the reduction potential and reversibility depend on the number of phenyl or methyl substituents at the macrocycle indicating a ligand-based reduction. Two nearly reversible cathodic waves were observed only for 6 at half-wave potentials -1.38 and -2.01 V versus Fc<sup>+</sup>/Fc. Fully reversible spectroelectrochemical response was observed in the in situ UV-vis-NIR spectroelectrochemistry of 6 (Figure 6), which contains the most extended  $\pi$ -system within the macrocycle. New absorption bands at 490 and 910 nm appear in the region of the first cathodic peak via isosbestic points and are typical for anion radicals with delocalized spin within the  $\pi$ -conjugated system. A broad slightly anisotropic intense EPR spectrum with g-value of  $g_{iso} = 2.0004$  characteristic for the ligand-based radical was observed confirming a purely ligand-based reduction and delocalized spin within the macrocycle.



**Figure 6.** In situ UV–vis–NIR spectroelectrochemistry of **6** in DMF/  $nBu_4NPF_6$  in a thin layer cell: potential dependence of UV–vis–NIR spectra with corresponding cyclic voltammogram (scan rate 20 mV s<sup>-1</sup>) in (a) forward and (b) backward scans.

Note that the redox behavior in the cathodic part is much more complex compared to the anodic oxidation, and this aspect is a matter of more extended study that will be reported separately. The results of these studies are in good agreement with DFT calculations, which show that frontier molecular orbitals of 4 are mainly ligand-centered. Both, 1e-reduction and 1e-oxidation are expected to take place at the ligands rather than at nickel(II) (vide infra).

**Theoretical Studies.** To get a deeper insight into the electronic structures of 1-6, their geometries were optimized using DFT (see Experimental Section). The structural parameters of the DFT-optimized structures match reasonably well with the experimental metrical parameters from singlecrystal X-ray diffraction data, as showcased for compounds 3-6 in Table S1.

In addition, the correlation of calculated electronic structure parameters relevant to the acceptance ( $\varepsilon_{LUMO}$  and electron affinity) of an electron with the experimentally measured redox behavior of **1**-**6** is quite good. One can see an almost perfect linear dependence in the case of reduction (see Figure 7a,b); the *R* factor is 0.9581 for  $\varepsilon_{LUMO}$  versus reduction potential (Figure 7a). In the case of electron affinity versus reduction potential, the *R* factor is 0.9819 (Figure 7b). The energies of all

studied species (neutral, single oxidized/reduced, and/or double reduced) and spin states are collected in Table 3. The correlation trend for oxidation (Figures 7c,d) is less linear than that for the reduction, with  $\mathbf{5}$  (presence of pyridine group) being the outlier, likely because the differences among the complexes occur in a considerably smaller potential window.

Following the B3LYP/6-311G\* calculation we found the singlet states to be preferred in the case of neutral <sup>1</sup>[Ni<sup>II</sup>L]<sup>0</sup> species and doublets in the case of  ${}^{2}[Ni^{II}L\cdot]^{-}$  and  ${}^{2}[Ni^{II}L\cdot]^{+}$ . According to the B3LYP/6-311G\* frontier orbitals and spin densities, shown in Figure 8 for 4, the first oxidation and reduction events are both mostly ligand-centered. However, the oxidation shows a partial contribution of the central  $\mathrm{Ni}^{\mathrm{II}}$ ion, which is reflected by the shapes and Ni atom populations of B3LYP/6-311G\* highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 4 (Figure 8a-d), as well as by the particular spin densities of the corresponding radical cation and radical anion (Figure 8e,f), albeit the B3LYP/6-311G\* calculations favor a ligand-centered redox process, unless the order of the closely degenerate HOMO and HOMO-1 is not reversed due to the choice of the functional used (vide infra).

Furthermore, the d-orbital Mulliken populations on Ni as well as the QTAIM and/or Mulliken charges and spins of Ni (see Table 4) of the neutral, oxidized, and reduced species remain almost constant, being in line with the interpretation of preferably ligand-centered redox processes. Nevertheless, according to experimental findings, the oxidation process (smaller effect of ligand substitution on the potential) as well as  ${}^{2}$ [Ni<sup>II</sup>L·]<sup>+</sup> itself (the EPR signal) are affected by the Ni ion. HOMO-1 is close in eigenvalue with HOMO, and it has a  $d_{xy}$ orbital population of 19%; hence, the choice of DFT functional might affect the frontier orbitals order. For instance, the BLYP functional HOMO has a 48% Ni character (not shown). In addition, the B3LYP/6-311G\* d-orbital populations shown in Table 4 agree well with crystal field theory (CFT) ordering of Ni<sup>II</sup> d-orbitals of square-planar  $(D_{4h})$  coordination geometry; that is, the CFT-ordered d-orbitals according to energy correlate with the population on a given d orbital.

Following the B3LYP/6-311G\* localized orbitals of all species in Table 4, one finds eight d electrons on Ni; hence, one can assign the formal oxidation state of nickel to 2+. An additional discrepancy with CFT is the removed degeneracy of  $d_{yz}$  and  $d_{xz}$  atomic orbitals (AOs) at the B3LYP/6-311G\* level of theory when considering the obtained populations. This is likely related to the fact that the macrocyclic ligand is not of square-planar ( $D_{4h}$ ) symmetry, and hence bonds along x and y axes are different. This is further confirmed by the QTAIM bond critical point (BCP) characteristics (see Table S2).

Calculated EPR B3LYP/6-311G\* and BLYP/6-311G\* *g*tensor parameters are shown in Table S3. The BLYP functional was utilized because of a closer agreement with the anisotropy of the oxidized species found experimentally. The reduced  ${}^{2}[4]^{-}$  species has *g*-tensor components closer to a free electron *g*<sub>e</sub> value. Still, the *g*<sub>xx</sub> component is below 2.000 what is in line with a small contribution of the central ion. In the case of the oxidized species  ${}^{2}[2]^{+}$ , the obtained electronic structure leads to an underestimated *g* value compared to the experiment (see Figure 5b), despite the BLYP functional choice, which leads to a larger contribution of the Ni ion. To improve the agreement with the larger anisotropy of  ${}^{2}[2]^{+}$  found experimentally, the HOMO  $\beta$  [eigenvalue -0.2769; 30.5% Ni(d) character] and



**Figure 7.** Correlation of theoretically determined parameters (a)  $\varepsilon_{LUMO}$ , (b) electron affinity, (c)  $\varepsilon_{HOMO}$ , and (d) ionization energy with the experimentally determined reduction  $E_{1/2}^{red}$  and oxidation  $E_{1/2}^{ox1}$  potentials of **1–6**.

Table 3. Total 6-311G	<sup>4</sup> Energies of All Studied	Species and Spin States
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		-	_	_			
charge	$M_{\rm S}$	1	2	3	4	5	6
0	1	-3250.378 52	-3633.922 22	-3825.693 84	-4017.4710	-3841.733 06	-3978.156 14
0	3	-3250.344 39	-3633.887 55	-3825.659 94	-4017.4367	-3841.674 92	-3978.113 09
-1	2	-3250.465 86	-3634.016 66	-3825.791 85	-4017.5709	-3841.84221	-3978.273 07
-1	4	-3250.429 49	-3633.980 68	-3825.756 25	-4017.534 99	-3841.806 52	-3978.2151
1	2	-3250.1861	-3633.728 73	-3825.500 58	-4017.2772	-3841.536 85	-3977.955 34
1	4	-3250.154 32			-4017.2447		-3977.905 22
2	1	-3249.947 67	-3633.493 66	-3825.266 43	-4017.0443	-3841.302 39	-3977.721 01
2	3	-3249.9452	-3633.492 11	-3825.264 29	-4017.0462	-3841.29971	-3977.720 66
<sup>a</sup> All values a	re in hartre	es. Spin multiplicity	is denoted $M_{\rm S}$				

LUMO  $\beta$  [eigenvalue -0.2680; 4.8% Ni(d) character] were rotated (BLYP<sup>rot</sup>) to calculate the *g*-tensor values, which lead to a further improvement in comparison to experiment. Nevertheless, the agreement is still not perfect; that is, the two largest *g*-components and the width of the spectrum are still underestimated. The largest anisotropy is found after the inclusion of solvent effects (COSMO – DCM) for the BLYP<sup>rot</sup> *g*-values. Similar results were also obtained for the <sup>2</sup>[4]<sup>+</sup> species, with the anisotropy and width of the spectrum being larger compared to <sup>2</sup>[2]<sup>+</sup>. The *g*-tensor is found ligandcentered in the case of <sup>2</sup>[6]<sup>+</sup>. Hence, the HOMO–LUMO rotation for <sup>2</sup>[6]<sup>+</sup> cannot be considered as appropriate. Although the HOMO/LUMO orbitals of <sup>2</sup>[6]<sup>+</sup> are closely degenerate, the dominant ligand character of the singly occupied molecular orbital (SOMO) is in agreement with the experimental evidence contrary to  ${}^{2}[2]^{+}$  and  ${}^{2}[4]^{+}$ . Even though the macrocyclic ligands in 1-6 create a strong ligand field favoring the formation of square-planar nickel(II) complexes and making further axial coordination of coligands unlikely, we observed dimeric associates in the crystal structure of **5** hold together by weak Ni…S contacts of 3.42 Å. Therefore, we decided to test the activity of 1-6 in catalytic cyclohexane oxidation reactions.

**Catalytic Studies.** In the present study, the MW-induced neat oxidation of cyclohexane to A/K oil (Scheme 2) was chosen as a benchmark reaction. Nickel(II) complexes 1-6 were tested as catalysts for the above reaction, using aqueous TBHP as oxidant.



Figure 8. (a–d) Frontier orbitals of  ${}^{1}[4]^{0}$  (eigenvalues are shown in parentheses; in hartrees), isosurface value is 0.06 e·bohr<sup>-3</sup> and (e, f) spin density of (e)  ${}^{2}[4]^{-}$  and (f)  ${}^{2}[4]^{+}$ , isosurface value is 0.002 e·bohr<sup>-3</sup>.

Table 4. Mulliken d-Orbital Populations of Different Species of 4 and MPA and QTAIM Charges and Spins of 4 in DCM

species	$d_{x^2-y^2}$	d <sub>xy</sub>	$d_{z^2}$	$d_{yz}$	d <sub>xz</sub>	$\mathbf{s}_{\sigma}$	$\mathbf{d}_{\mathrm{total}}$
<sup>1</sup> [4] <sup>0</sup>	1.05	1.66	1.85	1.86	1.93	0.57	8.36
<sup>2</sup> [4] <sup>-</sup>	1.04	1.67	1.84	1.87	1.93	0.61	8.35
<sup>2</sup> [4] <sup>+</sup>	1.08	1.62	1.86	1.87	1.93	0.53	8.36
		MPA			(	QTAIM	
		charge	large spin		charge		spin
<sup>1</sup> [ <b>4</b> ] <sup>0</sup>		1.02	0.00		0.97		0.00
<sup>2</sup> [4] <sup>-</sup>		0.98	-0.02		0.95	0.01	
2[4]+	<sup>+</sup> 1.05		-0.01			-0.01	

Scheme 2. Microwave-Assisted Neat Oxidation of Cyclohexane to A/K Oil with *tert*-Butylhydroperoxide Catalyzed by 1–6



The effect of several catalytic parameters, such as reaction temperature and time, catalyst, and oxidant amount, on the catalytic activity (in terms of turnover number (TON), turnover frequency (TOF), and/or yield) was investigated. The optimized reaction conditions were: 2 h of MW irradiation at 100 °C in the presence of 10  $\mu$ mol of catalyst, leading to a maximum A/K oil yield of 23% (Figure 9) with a TON value of 1.1 × 10<sup>2</sup>.

The ability of compounds 1-6 to catalyze the oxidation of cyclohexane follows the trend found for their reduction potentials (vide supra), with the total yields of cyclohexanol and cyclohexanone, obtained under the optimized assayed conditions, from 7 (for 1) to 23% (for 6) and TON from 37 to 113. The compound easiest to reduce, 6, exhibits the highest catalytic activity. The catalytic activity decreases with the decrease of reduction potential, with 1 exhibiting the most negative reduction potential and lowest A/K oil yield obtained. Thus, the significant effect of the substituents at the macrocycle suggests the reduction potential as an important factor for their catalytic behavior.

In fact, the cyclohexane oxidation mechanism appears to be of radical nature. One evidence results from the performed experiments to detect the formation of cyclohexyl hydroperoxide as a primary product, following a method proposed by Shul'pin: 53-59 the detected cyclohexanol amount significantly increased after addition of triphenylphosphine to the reaction mixture (due to the reduction of CyOOH by PPh<sub>3</sub>, with the formation of phosphane oxide) and a decrease in the amount of cyclohexanone. Moreover, the experiments involving the addition of the oxygen radical trap (Ph<sub>2</sub>NH) to the reaction mixture led to a significant yield drop of over 93%, when compared to the reaction performed under the same conditions in the absence of such a radical trap. Thus, the MW-promoted oxidation of neat cyclohexane catalyzed by the nickel(II) complexes 1-6 should proceed through a freeradical mechanism, where the availability of reducible Ni<sup>II</sup>L octaazamacrocyclic complexes (as proved by electrochemistry) by the hydroperoxide would be crucial for the oxidation to occur (see Scheme 3).<sup>28</sup> Consequently, the Ni-catalyzed formation of t-BuOO· and t-BuO· radicals is a key step for the occurrence of the C–H abstraction from the cyclohexane, leading to to the formation of cyclohexyl radical, the beginning of the cyclohexane conversion, that proceeds by a radical path to the desired products cyclohexanol and cyclohexanone. The involvement of t-BuOOH in reduction-based chemistry was evidenced by following the reaction of the latter with 6 by UV-vis and EPR spectroscopies. A very small amount of reduced 6 is clearly seen after addition of TBHP in Figure S8. EPR spin-trapping experiments with 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) spin trap and TBHP in the presence of 6 revealed higher amount of reactive radicals than in the absence of nickel(II) complex (Figure S9) attesting the catalytic activity of 6 with involvement of radical-based reactions. Note that similar behavior was reported previously for the systems with  $H_2O_2$ .<sup>70,71</sup>

As previously observed for other catalytic systems<sup>28,65–67</sup> the used low (25 W) power of MW irradiation provides a much more efficient synthetic method than conventional (nonpressurized refluxing) heating, allowing the fast achievement of significantly higher yields (e.g., for compound **6**, 23% A/K oil yield by 2 h of MW irradiation in comparison with 6.4% using an oil bath heating).

Our catalysts 1-6 are much more effective and selective than the [Ni(tpa)] (tpa = tris(2-pyridylmethyl)amine))<sup>68</sup> or the [Ni(OAc)<sub>2</sub>(H<sub>2</sub>O)(L<sup>tBu</sup>)] (L<sup>tBu</sup> = N,N-bis(2-pyridylmethyl)-N-{(1-tert-butyl-1H-1,2,3-triazol-4-yl)methyl}amine)<sup>69</sup> complexes, which require the much stronger *m*-chloroperbenzoic acid (*m*CPBA) as oxidant and lead to cyclohexanol,



Figure 9. Total yield of cyclohexanol and cyclohexanone obtained by MW-induced neat oxidation of cyclohexane with THBP catalyzed by the nickel(II) complexes 1-6 (10  $\mu$ mol) at 100 °C.

# Scheme 3. Reaction Mechanism of Catalyzed Oxidation of Cyclohexane in the Presence of Octaazamacrocyclic Nickel(II) Complexes

$$\begin{split} & [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{0} + t \cdot \mathrm{BuOOH} \rightarrow t \cdot \mathrm{BuOO^{\bullet}} + \mathrm{H^{+}} + [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{-} \\ & [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{-} + t \cdot \mathrm{BuOOH} \rightarrow t \cdot \mathrm{BuO^{\bullet}} + [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{0} + \mathrm{HO^{-}} \\ & t \cdot \mathrm{BuO^{\bullet}} + \mathrm{CyH} \rightarrow t \cdot \mathrm{BuOH} + \mathrm{Cy^{\bullet}} \\ & \mathrm{CyO^{\bullet}} + \mathrm{CyOO^{\bullet}} \\ & \mathrm{CyOO^{\bullet}} + t \cdot \mathrm{BuOOH} \rightarrow \mathrm{CyOOH} + t \cdot \mathrm{BuOO^{\bullet}} \\ & \mathrm{CyOOH} + [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{-} \rightarrow \mathrm{CyO^{\bullet}} + [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{0} + \mathrm{HO^{-}} \\ & \mathrm{CyOOH} + [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{-} \rightarrow \mathrm{CyOO^{\bullet}} + \mathrm{H^{+}} + [\mathrm{Ni}^{\mathrm{II}}\mathrm{L}]^{-} \\ & \mathrm{CyOO^{\bullet}} + \mathrm{CyH} \rightarrow \mathrm{CyOH} + \mathrm{Cy^{\bullet}} \\ & 2 \mathrm{CyOO^{\bullet}} + \mathrm{CyOH} \rightarrow \mathrm{CyOH} + \mathrm{Cy^{\bullet}} \\ \end{split}$$

cyclohexanone, and  $\varepsilon$ -caprolactone (from Baeyer–Villiger reaction of cyclohexanone with *m*CPBA) mixtures. They are also more efficient catalysts than the nickel(II) complexes of N-heterocyclic carbene (NHC) ligands *trans*-[NiX<sub>2</sub>(NHC)<sub>2</sub>] (X = Cl or I), which afford a maximum A/K-oil yield of 15%, with a cyclohexane-to-TBHP ratio of 1:14 and 12 h reaction time at 70 °C, thus in much more drastic conditions than those used in the present study.

# CONCLUSIONS

Stepwise template building of octaazamacrocyclic nickel(II) complexes 1-6 was possible due to symmetry nonequivalence of two end amine groups in *S*-methylisothiocarbohydrazide or *S*-methylisothiocarbohydrazidium iodide. This symmetry nonequivalence results from thiomethylation of thiol sulfur atom in thiocarbohydrazide due to the formation of a double bond and steric hindrance of one of the end NH<sub>2</sub> groups by SCH<sub>3</sub> group. For the same reason, the template condensation reaction of intermediate species **A** in Scheme 1 with benzoylacetone and 1-(4-pyridinyl)-butane-1,3-dione results mainly in the formation of one geometric isomer, the structure of which was confirmed by X-ray crystallography of **3** and **5**.

For relatively stable radical cations the rhombic EPR signal with a rather large *g*-tensor anisotropy, obtained at 110 K upon one-electron oxidation, indicates the formation of a ligand-centered radical with pronounced delocalization of the

unpaired spin into the orbitals of nickel ion. The EPR spectra are neither typical nickel(III) nor organic radical, in character, which indicates a system with a redox noninnocent ligand. The found redox behavior was further confirmed by the shapes of the HOMO and LUMO orbitals, visualization of spin densities, and population analysis.

Compounds 1-6 act as catalysts for the MW-induced and solvent-free oxidation (with aq TBHP) of cyclohexane, via a radical mechanism, affording selectively cyclohexanol and cyclohexanone and in good yields (up to 23%), as a promising alternative to the industrial aerobic process, which also operates at higher temperature. The catalytic activity was found to correlate well with the easy of reduction of the nickel(II) complexes with noninnocent macrocyclic ligands, with complex **6** as the most active in the series and easiest to reduce.

# ASSOCIATED CONTENT

# **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01700.

X-ray diffraction structure of S-methylisothiocarbohydrazidium iodide, details of crystal structures for 3-5and 6-2DMF, EPR spectra of  $[2]^+$  and  $[5]^+$ , details of DFT calculations (PDF)

#### **Accession Codes**

CCDC 1921435–1921438 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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# Notes

The authors declare no competing financial interest.

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