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Synthesis and Catalytic Activity of Square-Planar Ni(II) Complexes of Bis-N,N′-disubstituted Oxamides and Related Ligands for Epoxidation of Olefins

by G.X. Zheng[*], Q.F. Wang and S.L. Yan

School of Chemical Engineering, Jinan University, Jinan 250022, P. R. China

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Four new monomeric square-planar nickel(II) complexes of two bis-N,N′-disubstitute oxamides and related ligands have been prepared and characterized, namely $[NMe_4]_2[Ni(L)]\cdot xH_2O$, where L = dbopba = 3,5-dibromo-o-phenylenebis-(oxamate) and dbmeopba = 3,5-dibromo-o-phenylenebis-(N′-methyloxamidate), L = meopba = 4-methyl-o-phenylenebis-(oxamate) and memeopba = 4-methyl-o-phenylenebis-(N′-methyloxamidate). NMe_4 is the tetramethylammonium cation. Based on elemental analyses, IR and UV spectroscopies and molar conductance data, the complexes are proposed to have a square-planar structure. Their catalytic activities for aerobic epoxidation of olefins with co-oxidation of iso-butylaldehyde have been discussed.

Key words: square-planar nickel(II) complexes, synthesis, characterization, catalytic activity

The use of transition-metal complexes as catalysts for epoxidation reactions has received increased attention during the last decades [1–3], particularly by the interest in understanding reactions of biological importance, where the metal ion plays a central role [4]. It was found that the oxamide-metal complexes have high catalytic activity for aerobic epoxidation of olefins with co-oxidation of pivalaldehyde [5,6]. In this context we have report on synthesis of two bis-N,N′-disubstitute oxamides and related ligands. Four new monomeric square-planar nickel(II) complexes $[NMe_4]_2[Ni(L)]\cdot xH_2O$ were prepared, where L = dbopba = 3,5-dibromo-o-phenylenebis-(oxamate) and dbmeopba = 3,5-dibromo-o-phenylenebis-(N′-methyloxamidate), L = meopba = 4-methyl-o-phenylenebis-(oxamate) and memeopba = 4-methyl-o-phenylenebis-(N′-methyloxamidate), x = 4, 5. Their IR, electronic spectral and conductivity properties are also reported. Their catalytic activities for aerobic epoxidation of olefins with co-oxidation of iso-butylaldehyde have been discussed.

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[*] Author for correspondence.

EXPERIMENTAL

Preparation of 3,5-dibromo-1,2-phenylenediamine: 10 g of powder of iron was suspended in a mixture of water (100 mL) and ethanol (10 mL). 1 mL of 36% HCl was added to the stirred suspension, which was heated to 80°C. Then 5.92 g of 4,6-dibromo-2-nitrobenzenamine was added to the stirred mixture during 1 hr at the temperature of 80°C. The mixture was stirred at this temperature until the reaction was completed, then was cooled to 25°C and 50 mL of ethanol was added. The solid was filtered and the liquid solution was concentrated to 1/4 volume under reduced pressure. The liquid was cooled down and formed white micro-crystals were filtered off, washed with water and dried in vacuum. 3,5-Dibromo-1,2-phenylenediamine was obtained in a yield of 70% (3.72 g).

Preparation of H_2-dbopba: The diethyl ester of N,N′-3,5-dibromo-o-phenylene-bis-(oxamic acid) (H_2-dbopba) was prepared from ethyloxalyl chloride and 3,5-dibromo-1,2-phenylenediamine by similar our method [7].

Preparation of H_4-dbmeopba: A methanol solution (50 mL) of H_2-dbopba, 10 mmol, was treated with 30 mmol of methylamine (30% solution in methanol) at room temperature. The mixture was kept at 60℃ for 2 hours with vigorous stirring and the white precipitate was filtered off, washed with methanol and dried under vacuum. The yield of H_4-dbmeopba was 92%.

H_4-memeopba was prepared similarly except that diethyl ester of N,N′-4-methyl-o-phenylene-bis-(oxamic acid) (H_2-meopba) was used instead of diethyl ester of N,N′-3,5-dibromo-o-phenylene-bis-(oxamic acid) (H_2-dbopba).

Preparation of complexes: All four complexes were prepared in a similar fashion as typified by $[NMe_4]_2[Ni(dbopba)]\cdot 5H_2O$. To a suspension of 5 mmol H_2-dbopba in 100 mL methanol was added 25% methanol solution of $[NMe_4]OH$ (25 mmol). A methanol solution (40 mL) of $Ni(ClO_4)_2\cdot 6H_2O$, 5 mmol, was then added dropwise with stirring. The organic solution was filtered and reduced to 10 ml on a rotatory evaporator. The mixture was treated successively with ether and acetone to give a hygroscopic orange-yellow solid, which was rapidly filtered off and dried under vacuum. The yields are given in Table 1.

Table 1. Physical data of ligands and their compounds.

	Compound	Formula wt.	Colour	M.P. (°C)	Yield (%)	Λ_M (Ω^{-1} cm^2 mol^{-1})
(1)	H_2-meopba $C_{15}H_{18}N_2O_6$	322.32	white	178		
(2)	H_2-dbopba; $C_{14}H_{14}Br_2N_2O_6$	466.08	white	260		
(3)	H_4-memeopba $C_{13}H_{16}N_4O_4$	292.30	white	302		
(4)	H_4-medbopba $C_{12}H_{12}Br_2N_4O_4$	436.07	white	311		
(5)	$(Me_4N)_2[Ni(meopba)]\cdot 4H_2O$ $C_{19}H_{38}N_4O_{10}Ni$	541.22	orange-yellow	307	65	148
(6)	$(Me_4N)_2[Ni(dbopba)]\cdot 5H_2O$ $C_{18}H_{36}Br_2N_4O_{11}Ni$	703.00	orange-yellow	321	67	140
(7)	$(Me_4N)_2[Ni(memeopba)]\cdot 4H_2O$ $C_{21}H_{44}N_6O_8Ni$	567.31	orange-yellow	315	60	143
(8)	$(Me_4N)_2[Ni(medbopba)]\cdot 4H_2O$ $C_{20}H_{40}Br_2N_6O_8Ni$	711.07	orange-yellow	325	64	140

General procedure for aerobic epoxidation of alkene: Iso-butylaldehyde (10 mmol) and unactivated alkene (5 mmol) were added to a stirred solution of $[NMe_4]_2[Ni(L)]\cdot xH_2O$ (0.1 mmol) in anhydrous acetonitrile 30 mL. The mixture was stirred at ambient temperature (25℃) under dioxygen balloon for 8–10 h. The solvent was evaporated *in vacuo*, and the residue was dissolved in ether. The ether layer was washed with saturated $NaHCO_3$ solution (3×15 mL), brine solution (2×15 mL), and water (2×20 mL). Drying with $MgSO_4$ and evaporation yielded a residue. The obtained epoxide and unreacted alkene were separated by flash column chromatography on silica gel. The yields are listed in Table 2. All compounds exhibited spectral data consistent with their structures.

Table 2. Results for the epoxidation alkenes with dioxygen and iso-butylaldehyde catalyzed by nickel complexes.

Catalyst	Yield (%) Epoxide of styrene from styrene	Yield (%) Epoxide of stilbene from *trans*-stilbene	Yield (%) Epoxide of stilbene from *cis*-stilbene	Yield (%) Epoxide of cyclohexene from cyclohexene
$(Me_4N)_2[Ni(meopba)]\cdot 4H_2O$	80(4h)	94(2h)	32(12h)	35(12h)
$(Me_4N)_2[Ni(dbopba)]\cdot 5H_2O$	78(4h)	92(2h)	28(12h)	37(12h)
$(Me_4N)_2[Ni(memeopba)]\cdot 4H_2O$	76(4h)	85(2h)	25(12h)	33(12h)
$(Me_4N)_2[Ni(medbopba)]\cdot 4H_2O$	75(4h)	84(2h)	26(12h)	30(12h)

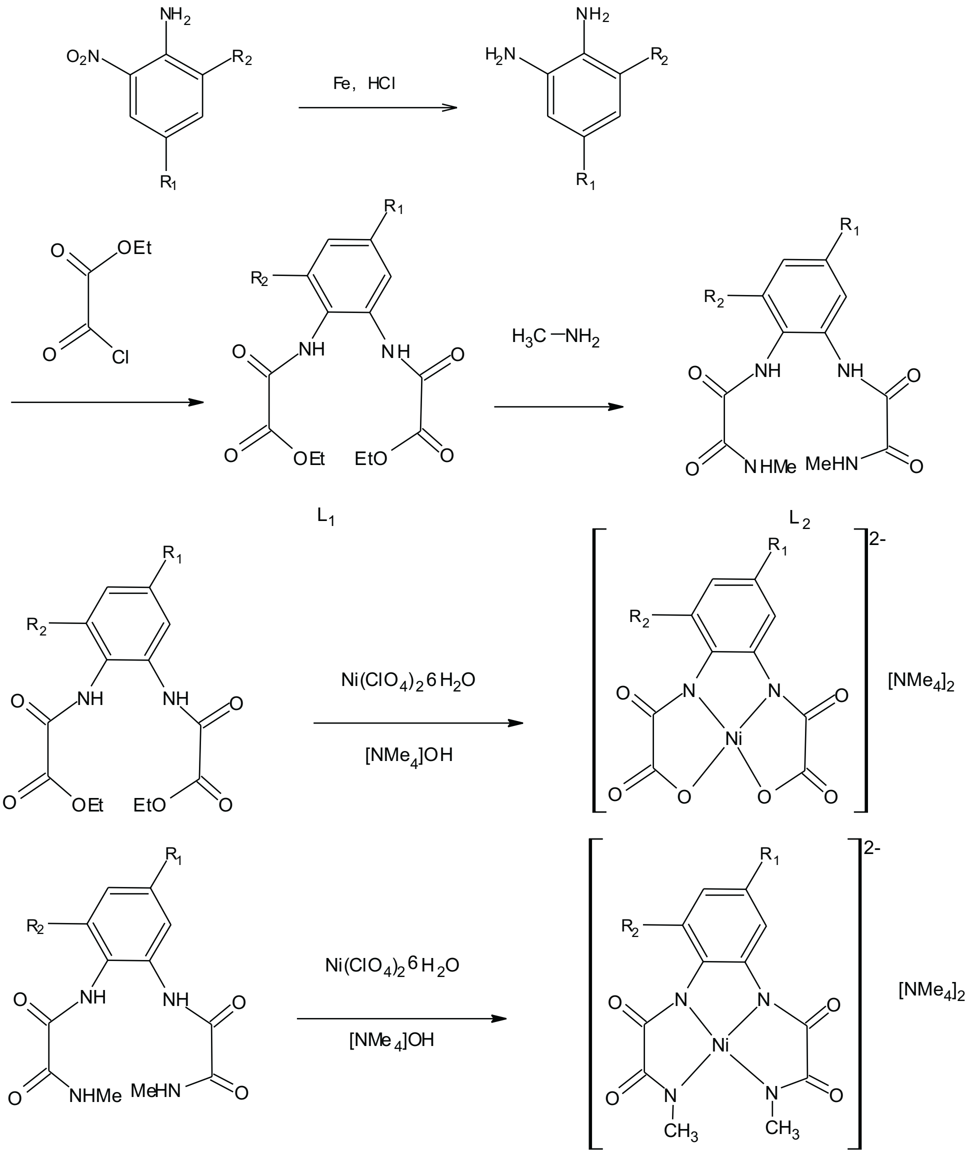
Physical measurements: Elemental analyses were carried out with a Perkin-Elmer 2400 elemental analyzer. Metal contents were determined by EDTA titration. The electronic spectra were recorded on a Perkin-Elmer Hitachi UV-3000 spectrophotometer in DMF (Table 3). The molar conductance was measured with a DDS-11A conductivity meter (in 10^{-3} mol dm^{-3} DMF solution). Infrared spectra of the complexes were recorded on a Bio-Rad FTS-165 spectrometer in KBr pellets (Table 3). ^{1}H NMR spectra of complexes were recorded by JEOL-90Q spectrometer in $CDCl_3$ solvent with TMS as an internal reference. The melting points of the complexes were determined by an XT-1 micro-melting point apparatus (Beijing, China).

RESULTS AND DISCUSSION

Synthesis route and composition: The preparation of ligands and their complexes reaction are presented in Scheme 1.

Indeed, elemental analyses and physical data (see Table 1) indicate that the reaction of ligands with $Ni(ClO_4)_2\cdot 6H_2O$ and NMe_4OH yielded the nickel(II) complexes of the general formula $[NMe_4]_2[Ni(L)]\cdot xH_2O$, as expected. The molar conductance values fall in the expected range for 1:2 electrolytes [8]. The complexes are stable in air and insoluble in ether, chloroform and benzene. They are soluble in DMF, DMSO, water and methanol.

IR spectra: The infrared spectra of the ligands and complexes are shown in Table 3. The $\nu_{N\text{-}H}$ strong bands of the ligands (1) and (2) occur at 3258~3259 cm^{-1}, but in the ligands (3) and (4) because of existing two kinds of amide of oxamide, two strong $\nu_{N\text{-}H}$ vibration absorptions appear at 3324–3281 cm^{-1}. Those bands were not observed in the spectra of the nickel(II) complexes. This fact has been attributed to the coordination of the nitrogen-donor of oxamide to nickel(II). In addition, the $\nu_{(C=O)}$ vibration of ligands were shifted to lower frequencies when formed the nickel(II) complexes, which also indicates the coordination of the nitrogen-donor of oxamide to nickel(II) to form π delocalization of the carbonyl double bond of the NCO amide fragment [9]. Within two oxamato moieties and oxamido ones, the two vibrational modes $\nu_{1(CO)}$ and $\nu_{7(CO)}$ are red shifted {*e.g.* for $(Me_4N)_2[Ni(meopba)]\cdot 4H_2O$ (5) occurs at 1615–1662 cm^{-1} (oxamato) and $(Me_4N)_2[Ni(memeopba)]\cdot 4H_2O$ (7) occurs at 1608–1590 cm^{-1}



R_1 = Me, R_2 = H, L_1 = H_2-meopba; R_1 = R_2 = Br , L_1 = H_2-dbopba;
R_1 = Me, R_2 = H, L_2 = H_4-memeopba; R_1 = R_2 = Br , L_2 = H_4-medbopba;

Scheme 1. Synthesis reaction of ligands and their complexes.

(oxamido)} following the sequence (5) > (7) and (6) > (8). These changes occurred because the oxamto moieties were replaced by oxamido ones in their ligands.

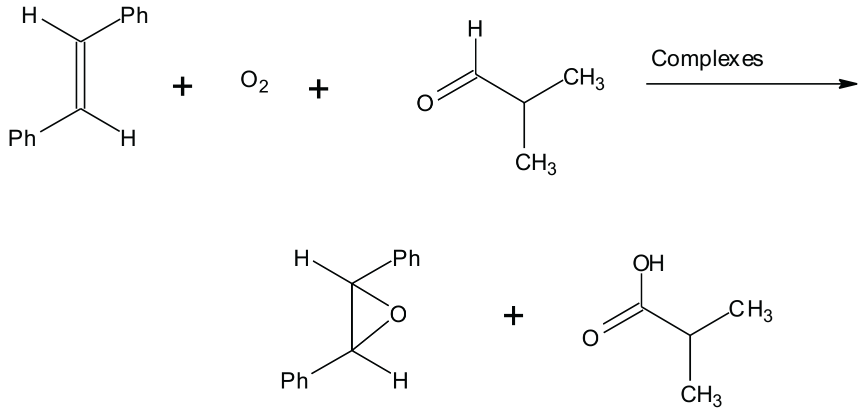
Furthermore, the noticeable shifts are observed for the infrared frequencies of the C=O amide group from complexes (5) and (6), (7) and (8). $\nu_{1(CO)}$ and $\nu_{7(CO)}$ were shifted to lower frequency for 5 cm^{-1} probably due to the presence of two bromine atoms in the ligands (6) and (8).

Table 3. Important infrared and electronic spectral data for the complexes.

	Compound	IR spectra (cm^{-1})					UV data in DMF		
		ν(O–H)	ν(N–H)	ν(N–C=O)	ν(O–C=O)	ν(C–O)	λ_{max} (nm) (log ε)		
(1)	H_2-meopba		3259 s	1690 s	1740 s	1328 m			
(2)	H_2-dbopba		3258 s	1687 s	1741 s	1327 m			
(3)	H_4-memeopba		3323 s, 3279 s	1689 s, 1660 s					
(4)	H_4-medbopba		3324 s, 3281 s	1683 s, 1658 s					
(5)	$(Me_4N)_2[Ni(meopba)] \cdot 4H_2O$	3593 s		1615 s	1662 s	1331 m	251 (4.2)	350 (1.9)	463 (0.8)
(6)	$(Me_4N)_2[Ni(dbopba)] \cdot 5H_2O$	3597 s		1610 s	1651 s	1338 m	257 (4.1)	358 (1.8)	469 (0.7)
(7)	$(Me_4N)_2[Ni(memeopba)] \cdot 4H_2O$	3475		1608 s, 1590 s			253 (3.0)	354 (1.3)	412 (0.5)
(8)	$(Me_4N)_2[Ni(medbopba)] \cdot 4H_2O$	3477 s		1603 s, 1586 s			256 (3.2)	356 (1.1)	415 (0.6)

Electronic spectra: The electronic spectra of all complexes are listed in Table 3. The electronic absorption spectra of the nickel(II)–oxamate complexes (5) and (6) in DMF solutions show a similar pattern consisting of an intense band in the UV region centered at 250 nm, with two distinct shoulders located at 356–358 and 463–469 nm. The nickel(II)–(N′-methyloxamidate) complexes (7) and (8) have three similar absorptions located at 255–256 nm, 354–356 nm and 412–415 nm. The high-energy peaks 255–256 nm and 354–356 nm, which also appear in the spectrum of the ligands, were commonly assigned to π-π* transitions within the aromatic ring of the ligands. The weak shoulders on the low-energy tail of this intra-ligand absorption band at 412–469 nm may correspond to a charge transfer transitions of the type oxamate→nickel(II) [for complexes (5) and (6)] or (N′-methyloxamidate)→ nickel(II) [for complexes (7) and (8)]. The position of third less intense band is different for oxamate→nickel(II) [(5) and (6) 463–469 nm] and (N′-methyloxamidate)→nickel(II) [(7) and (8) 412–415 nm]. If the relative positions and intensities of these two transitions remain constant, the position of the maximum for the band envelope is a measure of the ligand-field strength and, hence, indicative of the crystal-field stabilization energy [9]. So, the observed blue shift in the visible absorption maxima along this series of nickel(II) complexes is in agreement with the stronger ligand field associated with nitrogen-donor ligands rather than oxygen ones, *e.g.* the NiN_2O_2 chromophore for complexes (5) and (6), and NiN_4 for complexes (7) and (8).

Catalytic activity for epoxidation of alkene: In order to uncover the potential catalytic reactivity of those new complexes, it was examined the ability to catalyse the epoxidation of some representative distubstituted alkenes using dioxygen as oxidant in the presence of iso-butylaldehyde. The results are summarized in Table 2. It was found that the complex $(Me_4N)_2[Ni(memeopba)]\cdot 4H_2O$ catalyses the epoxidation of *trans*-stilbenes by oxygen and iso-butylaldehyde in acetonitrile with yield 85% of the corresponding epoxide. Similar results were obtained with complexes (5), (6) and (8). By contrast, the yield of corresponding epoxide of *cis*-stilbene is only about 25–32%, even after a total reaction time of 12 h, indicating that the catalytic epoxidation is greatly stereo dependent. The cyclohexene was oxidized by similar method to form epoxide with a yield of about 30–37%. For all the olefins, however, epoxides were the only oxidation products as confirmed by ^1H NMR spectroscopy. ^1H NMR of *trans*-stilbene oxide: ($CDCl_3$) δ: 3.86 (s, 2 H, 2 × -CH-), 7.26–7.45 (m, 10 H, 2 × C_6H_5-); styrene oxide: δ: 3.80 (t, 1 H, -CH-), 2.81 (d, 2 H, -CH_2-), 7.24–7.40 (m, 5H, C_6H_5-). No traces of corresponding ketone or alcohol were detected for the epoxidation of cyclohexene which is typically regarded as good substrate to check for competition of alkenes vs. allylic oxidation. This observation suggests that typical free radical intermediates are not directly involved as potential epoxidizing agents. The catalytic epoxidation reaction is represented by Scheme 2.



Scheme 2. Catalytic epoxidation reaction.

CONCLUSIONS

Based on the composition of these complexes, their IR and electronic spectra, conductivity measurements, and the crystal structure of the analogous complex [10], these complexes are proposed to have a square-planar nickel(II) complexes structure shown in Scheme 1. Four new monomeric square-planar nickel(II) complexes catalyse the epoxidation of aromatic substituted olefins with molecular oxygen/iso-butylaldehyde with a good yield. The highly selective and effective catalytic system offers convenient and promising applications in synthesis.

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