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Research paper

Synthesis and characterization of a series of acylpyrazolone transition metal complexes: Crystal structures and catalytic performance in the epoxidation of cyclooctene

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ARTICLE INFO	A B S T R A C T
Keywords:	A series of transition metal complexes of 4-acetyl-3-methyl-1-phenyl-2-pyrazoline-5-one with Ni(II), Cu(II), Fe
Pyrazolone	(III) and Mn (II) central metal ions have been synthesized and characterized by X-ray crystallography, UV-Vis
Epoxidation	and FTIR spectroscopy, and elemental analysis. The complexes were used as a catalyst for epoxidation of cy-
Transition metal complexes	clooctene with tert-butylhydroperoxide. Various parameters, including catalyst type and amount, solvent type
Cyclooctene	and amount, oxidant/substrate ratio and time, have been optimized. The highest catalytic activity was found for
Crystal structure	Cu(II) complex at the optimized conditions. Very high selectivity for the epoxide product (cyclooctene oxide) was also obtained

1. Introduction

Transition metal complexes with pyrazolone derivatives have shown interesting chemical and physical properties and have attracted researcher attention [1–7]. Pyrazolones are very important due to their wide applications in several fields in pharmacology and biology due to their antibacterial, antimicrobial, antifungal and antioxidant, antitumor and anti-inflammatory activities [8-16]. They have also found applications in catalysis, laser technology, chromatographic materials, and in the petrochemical industry [17-20]. The tautomerism of such compounds is also a challenging field of study due to its importance in chemical reactivity. Most of these ligands show enol-keto tautomerism to cause different structures and spectroscopic properties [20-22]. The catalytic potential of several pyrazolone-based ligands has been investigated in various organic transformations. Marchetti and coworkers have recently reviewed the applications of pyrazolone-based transition metal complexes [2]. They have also reviewed acylpyrazolone ligands and their transition metal complexes [3]. According to their review and our literature survey, most of such complexes have been used in polymerization transformations, oxidation reactions and coupling reactions.

In the present work, we report the synthesis and characterization of a series of Ni(II), Cu(II), Fe(III) and Mn (II) transition metal complexes with 1-phenyl-3-methyl-4-acetyl-2-pyrazoline-5-one (PMAP). All of the complexes were characterized by multiple techniques including FTIR, UV–Vis, single-crystal X-ray crystallography, and elemental analysis. Catalytic reactivity of the complexes has been examined in the epoxidation of cyclooctene using *tert*-butylhydroperoxide (TBHP) as oxidant. Different parameters affecting the catalytic reactivity, including catalyst type and amount, solvent type and amount, oxidant/substrate ratio, and time, was optimized. High catalytic activity was observed mainly for the Cu(II) complex. Very high epoxide selectivity was also obtained.

2. Experimental

All the starting materials and solvents were purchased from commercial sources and were used as received. The FT-IR spectra were obtained as KBr plate using a Shimadzu 8400S FT-IR instrument in the range of 4000–400 cm⁻¹. Melting points were obtained on a Thermoscientific 9100 apparatus by using the simple capillary tube method. UV–Vis spectra were obtained on a Shimadzu UV-1650 PC spectrophotometer in DMSO solution. Elemental analysis was performed on a Perkin-Elmer 2400II CHNS-O analyzer. The structures of the products were confirmed unambiguously by single-crystal X-ray analysis. Gas chromatography (GC) analyses were carried out with a Capillary Bp-10 column on a GC-17A Shimadzu instrument equipped with an FID detector working at 280 °C.

2.1. Synthesis of 1-phenyl-3-methyl-4-acetyl-2-pyrazoline-5-one (PMAP)

This ligand was synthesized following the previously reported

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procedure [21]. In a typical experiment, calcium hydroxide (162 mmol, 12 g) was added slowly to 80 mL 1,4-dioxane solution of 3-methyl-1phenyl-2-pyrazoline-5-one (86 mmol, 15 g) with gentle heating and stirring. After 10 min, 10 mL of acetyl chloride was added dropwise during 1–2 min. An orange paste-like product appeared, and the mixture was refluxed for 1 h. The reaction mixture was then cooled on an ice bath. 200 mL of cold hydrochloric acid (2 M) was then added to the reaction mixture, followed by a continuous stirring until cream color crystals appeared. The crystals were collected with a Buchner funnel and were washed with a copious amount of water. Yield: 12.6 g. 84%. IR (cm⁻¹): 2933, 1612, 1593, 1544, 1496, 1458, 1436, 1363, 1330, 1087, 767.

2.2. Synthesis of complex (1)

10 mL methanolic solution of manganese(II) acetate anhydrate (1.00 mmol, 0.17 g) was added to 15 mL methanolic solution of PMAP (2.00 mmol, 0.43 g) and the reaction mixture was refluxed for 5 h. The resulting precipitate was collected with a Buchner funnel and dried at room temperature. Pure crystals suitable for X-ray crystallography were obtained by recrystallization from DMF and methanol after about 3 weeks. Yield: (0.42 g, 66%). Selected IR (cm⁻¹): 2934, 2923, 1649, 1616, 1591, 1581, 1539, 1490, 1465, 1365, 1344, 1251, 1110, 748, and 514. UV–Vis. 10⁻⁴ M solution in DMSO [λ_{max} nm, (ε M⁻¹cm⁻¹)]: 216 (84200), 246 (36000). Anal. Calcd. (Found) for C₃₀H₃₆MnN₆O₆: C; 57.00 (56.91), H; 5.70 (5.64), N; 13.30 (13.39).

2.3. Synthesis of complex (2)

This complex was prepared following a similar procedure as described for (1) except Iron(II) chloride tetrahydrate (1.00 mmol, 0.20 g) was used instead of manganese(II) acetate anhydrate. Recrystallization from DMF and methanol afforded 0.56 g, 80%, of pure crystals of the target complex suitable for X-ray crystallography. Selected IR (cm⁻¹): 2922, 1606, 1595, 1575, 1535, 1487, 1442, 1382, 1085, 759, and 694. UV–Vis. 10⁻⁴ M solution in DMSO [λ_{max} nm, (ε M⁻¹cm⁻¹)]: 216 (92000), 244 (31800), 350 (6600), 446 (2780). Anal. Calcd. (Found) for C₃₆H₃₃FeN₆O₆: C; 61.58 (61.50), H; 4.70 (4.75), N; 11.97 (12.05).

2.4. Synthesis of complex (3)

This complex was also prepared following a similar procedure as described for **(1)** except copper(II) perchlorate hexahydrate (1.00 mmol, 0.37 g) was used instead of manganese(II) acetate anhydrate. Recrystallization from methanol yielded 0.44 g, 89%, of pure crystals suitable for single-crystal X-ray crystallography. Selected IR (cm⁻¹) 3066, 1606, 1593, 1575, 1541, 1498, 1465, 1438, 1380, 1352, 1230, 1085 and 756. UV–Vis. 10⁻⁴ M solution in DMSO [λ_{max} nm, ($\epsilon M^{-1}cm^{-1}$)]: 218 (91600), 268 (17900), 340 (1000), 742 (80). Anal. Calcd. (Found) for C₂₄H₂₂CuN₄O₄: C; 58.30 (58.22), H; 4.45 (4.38), N; 11.34 (11.40).

2.5. Synthesis of complex (4)

This complex was prepared following a similar procedure as described for **(1)** except nickel(II) acetate tetrahydrate (1.00 mmol, 0.25 g) was used instead of manganese(II) acetate anhydrate. Recrystallization from methanol afforded 0.44 g, 78%, of pure crystals of the target complex suitable for X-ray crystallography. Selected IR (cm⁻¹) 3124, 3110, 1620, 1596, 1583, 1504, 1490, 1467, 1458, 1365, 1344, 1083, 748, and 449. UV–Vis. 10^{-4} M solution in DMSO [λ_{max} nm, (ϵ M⁻¹cm⁻¹)]: 216 (88300), 246 (21500), 342 (7700), 406 (1 5 0), 675 (50). Anal. Calcd. (Found) for C₂₆H₃₀N₄NiO₆: C; 56.40 (56.31), H; 5.42 (5.47), N; 10.12 (10.18).

2.6. X-ray crystallography

A single crystal of (2) of size $0.06 \times 0.03 \times 0.02 \text{ mm}^3$ and a single crystal of 3 of size $0.06 \times 0.04 \times 0.04 \text{ mm}^3$ were used for X-ray diffraction study at 95 K on a SuperNova four-circles diffractometer equipped with a CCD Atlas S2 detector, using the mirrors-collimated Cu-K α radiation ($\lambda = 1.54184 \text{ Å}$) from a micro-focus tube, and a Cryostream 800 + chiller. A larger single crystal of (1) of size $0.15 \times 0.10 \times 0.07 \text{ mm}^3$ and a single crystal of (4) of size $0.18 \times 0.14 \times 0.11 \text{ mm}^3$ were used for X-ray diffraction study at 120 K on a Gemini four-circles diffractometer equipped with a CCD Atlas S2 detector, using the mirrors-collimated Cu-K α radiation ($\lambda = 0.71073 \text{ Å}$) from a classical tube, and a Cryojet 5 chiller. The temperatures used for measurement were the lowest economic values reachable on both instruments. The crystal structures were solved by charge flipping with the Superflip [23] program and refined with the Jana2006 program package [24]. The refinement was carried out against all reflections.

The structure determinations of all compounds were straightforward; no disorder was found. H atoms attached to carbon were kept in the geometrically correct positions with a C–H distance of 0.96 Å. In the compound of 4, the hydrogen atoms connected to oxygen atoms were found in difference Fourier maps and refined freely. The crystal of (3) was twinned, with refined domain fractions equal to 0.8335 (9):0.1665 (9). The molecular structure plots were generated using Diamond 3 [25]. The crystallographic data and structure refinements for all compounds are summarized in Table 1.

2.7. General oxidation reactions

The synthesized complexes were used as a catalyst for oxidation of cyclooctene by TBHP as an oxidant in different reaction conditions. In the absence of the complexes, a minimal amount of oxidation products was observed. The progress of the reactions was monitored by GC (Gas chromatography). The conversion percentages (%) were calculated according to the Eq. (1) in which C_i is the initial and C_f is the final concentration of cyclooctene substrate. Selectivity was also calculated according to Eq. (2) [26]. The catalytic reactions were performed in quadruplicate and the results are the average of the obtained data.

$$Conversion\% = \frac{C_i - C_f}{C_i} \times 100$$
(1)

Selectivity% =
$$\frac{C_{epoxide}}{C_{totalproducts}} \times 100$$
 (2)

2.7.1. Oxidation of cyclooctene in solvent

In a typical experiment, $10 \,\mu$ mol of a catalyst was dissolved in $10 \,m$ L of freshly distilled methanol, and then, $10 \,m$ mol of cyclooctene and 20 mmol of TBHP were added. The reaction mixture was refluxed while being stirred, and the reaction progress was monitored at 60 min intervals.

2.7.2. Solvent-free oxidations

 $10\,\mu mol$ of the catalysts, $10\,mmol$ of cyclooctene, and $20\,mmol$ of TBHP were refluxed, and the progress of the reaction was monitored every $60\,min$ by GC.

3. Results and discussions

3.1. Synthesis of the complexes

All of the complexes were readily prepared from the reaction of metal salts with the PMAP ligand. Complex (2) was prepared from the reaction of $FeCl_2 \cdot 4H_2O$ with PMAP. Aerobic oxidation has occurred and Fe(II) ion has been oxidized to Fe(III) upon exposure to air. The same complex has been reported previously in which the title complex was

Table 1

Crystal data and final refinement details.

Crystal data	Complex (1)	Complex (2)	Complex (3)	Complex (4)
Chemical formula	C ₃₀ H ₃₆ MnN ₆ O ₆	C ₇₂ H ₆₆ Fe ₂ N ₁₂ O ₁₂	C24H22CuN4O4	C ₂₆ H ₃₀ N ₄ NiO ₆
Mr	631.6	1403.1	494	553.2
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	P21/n	P_{1}^{-}	P_{1}^{-}	P21/c
Z	2	2	1	4
Temperature (K)	120	95	95	120
Unit cell dimensions				
a (Å)	8.7828 (3)	9.2630 (3)	6.4811 (3)	16.1377 (5)
b (Å)	17.1305 (6)	18.2874 (6)	7.1952 (3)	8.7590 (2)
c (Å)	9.9907 (3)	20.6851 (7)	11.4811 (9)	19.1441 (6)
α (°)	90	71.394 (3)	93.540 (5)	90
β (°)	102.028 (3)	85.959 (3)	97.432 (6)	110.237 (3)
γ (°)	90	83.585 (3)	96.561 (4)	90
V (Å ³)	1470.14 (9)	3297.8 (2)	525.83 (5)	2538.98 (14)
$\mu ({\rm mm}^{-1})$	4.11	4.14	1.82	1.52
Crystal size (mm ³)	0.15 imes 0.10 imes 0.07	0.06 imes 0.03 imes 0.02	0.06 imes 0.04 imes 0.04	$0.18 \times 0.14 \times 0.11$
T_{\min}, T_{\max}	0.738, 1	0.969, 1	0.987, 1	0.842, 1
Measured reflections	11,536	20,221	3597	16,810
Independent reflections	2633	12,817	3346	4550
Observed reflections $[I > 3\sigma(I)]$	2462	8680	2409	4114
R _{int}	0.023	0.040	0.028	0.024
$R[F2 > 3\sigma(F2)]$	0.025	0.043	0.039	0.031
wR(F2)	0.074	0.123	0.122	0.090
$S^{1)}$	1.42	1.22	1.40	1.61
No. of parameters	196	883	152	340
Δρmax, Δρmin (e Å $^{-3}$)	0.21, -0.24	0.38, -0.45	0.38, -0.43	0.18, -0.44

1) Refinement program Jana2006 does not refine the weighting scheme. Therefore, S is based on weights from the experiment and usually is fairly above 1.

prepared from Fe(NO₃)₃·9H₂O [27].

3.2. Description of the crystal structures

3.2.1. Description of the crystal structure of (1)

Molecular structure of the complex (1) is shown in Fig. 1 with the common atom numbering scheme. Crystallography data and final structural refinement parameters are summarized in Table 1. Selected bond lengths and angles are also collected in Tables 2 and 3, respectively. Complex (1) is neutral containing two monoanionic 4-acetyl-3-



Fig. 1. Molecular structure of the complex (1) with an atom numbering scheme common for all reported complexes. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Symmetry code (i) -x, 1 - y, -z.

methyl-1-phenyl-5-pyrazolonato ligands (hereinafter named pyrazolonato) and two dimethylformamide ligands coordinated to the central Mn(II) ion located in the crystallographic inversion center.

The two pyrazolonato ligands take the enol tautomeric form and they are deprotonated on the OH group on the pyrazole ring. The geometry around the central metal ion is pseudo-octahedral with the two OO' type pyrazolonato ligands in the basal plane of the octahedron in trans form, and two DMF molecules coordinated in apical positions through their oxygen atoms. It could also be seen that the two pyrazolonato ligands are in anti configuration with respect to the enolato oxygen of the pyrazoline ring (i.e. O3 and O3ⁱ as shown in Fig. 1). According to Table 1, the two Mn-O1 and Mn-O3 bond distances are almost equal (2.1539 (9) and 2.1579 (8) Å). Besides, the two C1-O1 and C4-O3 bond distances (1.2556 (15) and 1.2642 (15) Å) are also almost equal, which implies that the two carbonyl groups are similar. The other two Mn-O bond distances are longer than the basal Mn-O bond distances (Mn-O2: 2.2107 (9) Å) which implies a z-out Jahn-Teller distortion and is usual for Mn(II) octahedral complexes [28]. The inversion center at the position of Mn(II) causes the exact location of the central metal ion on the basal plane, and 180° of trans O-Mn-O bond angles. All of the bond distances and bond angles are in the same range as those of the previously reported similar complexes [29,30].

3.2.2. Description of the crystal structure of (2)

Fig. 2 shows one molecule of the complex (2) with the same atom numbering scheme as used for the complex (1). The asymmetric unit of the complex (2) consists of two crystallographically independent, but chemically identical and geometrically very similar molecules. The complex is neutral with three monoanionic pyrazolonato ligands coordinated to the central Fe(III) metal ion. Like in the complex (1), the ligands are deprotonated from the OH group of the pyrazole ring. The coordination geometry of the metal center is distorted octahedral, and ligands are coordinated in a *facial* coordination geometry with respect to the enolato oxygen of the pyrazoline ring (i.e. O2, O4 and O6 in Fig. 2). The average Fe-O bond length from the pyrazolonato oxygen atoms, i.e. Fe1-O2, Fe1-O4 and Fe1-O6 (1.977 Å) is slightly shorter than the other Fe-O average bond lengths (2.034 Å). This is in contrary to those of complex (1) in which the average bond lengths from different

Table 2

Selected bond lengths (Å) around the central metal ions.

Complex (1)		Complex (2)		Complex (3)		Complex (4)	
Mn1-O2	2.1539 (9)	Fe2-07	2.008 (2)	Cu1-O1	1.9319 (19)	Ni1-02	1.9966 (12)
Mn1-O2 ⁱ	2.1539 (9)	Fe2-O9	2.045 (2)	Cu1-O1 ⁱ	1.9319 (19)	Ni1-O1	2.0386 (9)
Mn1-O2	2.2107 (9)	Fe2-O8	1.987 (2)	Cu1-O2	1.9171 (17)	Ni1-04	2.0107 (9)
Mn1-O2 ⁱ	2.2107 (9)	Fe2-O10	1.982 (2)	Cu1-O2 ⁱ	1.9171 (17)	Ni1-05	2.0842 (12)
Mn1-O3	2.1579 (8)	Fe2-O11	2.035 (2)			Ni1-O3	2.0314 (12)
Mn1-O3 ⁱ	2.1579 (8)	Fe2-O12	1.977 (2)				
		Fe1-O6	1.965 (2)				
		Fe1-O5	2.017 (2)				
		Fe1-O4	1.979 (2)				
		Fe1-O2	1.986 (2)				
		Fe1-O1	2.035 (2)				
		Fe1-O3	2.049 (2)				

oxygen atoms of the chelating ligands were almost equal. On the other hand, the average C–O bond lengths on the pyrazolone rings (1.278 Å) are almost similar to the average C–O bond lengths of the acetyl groups (1.268 Å) which indicates that the negative charge is delocalized on the two oxygen atoms. The trans and cis O-Fe-O bond angles substantially deviate from the ideal 180° and 90°, respectively, which is another evidence for the distortion from the ideal octahedron. All of the bond lengths and bond angles are similar to those of the previously reported similar complexes [27,31-32]. The crystal structure of the same complex was previously reported in [27] as a monoclinic structure with space group Cc. The Herein reported complex is a triclinic isostructural compound with P_1^- space group. The two structures were compared using CrystalCMP software [33] which showed that the two complexes have totally different packing and hence, the different structures are the result of this difference (see Fig. S1).

3.2.3. Description of the crystal structure of (3)

The synthesis of the title complex was reported previously, but without crystal structure [34]. Fig. 3 shows the molecular structure of the complex (3) with a common atom numbering scheme. This complex is also neutral in which two pyrazolonato ligands are coordinated to the central Cu(II) ion in the anti configuration with respect to the enolato oxygen of the pyrazoline ring (i.e. O2 and $O2^{i}$, see Fig. 3). The geometry around the central metal ion is square planar, and the central metal ion located at en inversion center lies almost exactly on the plane formed by the four coordinating oxygen atoms. The two different Cu-O bond lengths are similar, and the two different C-O bond lengths, i.e. C1-O1 (1.267 (3) Å) and C4-O2 (1.280 (3) Å) are also similar which is an indication of the delocalization of the negative charge on the two different oxygen atoms. All of the bond lengths and bond angles are similar to those of the previously reported similar complexes [35,36].

Table	3
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Selected	bond	angles	around	the	central	metal	ion.



Fig. 2. Molecular structure of complex (2) with an atom numbering scheme common for all reported complexes. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

3.2.4. Description of the crystal structure of (4)

Fig. 4 shows the molecular structure of complex (4) with a common atom numbering scheme. As could be seen from Fig. 4, the molecule of

Complex (1)		Complex (2)		Complex (3)		Complex (4)	
O1-Mn1-O1 ⁱ	180.0 (5)	O6-Fe1-O5	90.15 (9)	O1-Cu1-O1 ^a	180.0 (5)	02-Ni1-O1	91.07 (4)
01-Mn1-O3	85.05 (3)	O6-Fe1-O4	88.29 (9)	01-Cu1-O2	85.75 (8)	02-Ni1-O4	88.36 (4)
O1-Mn1-O3 ⁱ	94.95 (3)	O6-Fe1-O2	97.43 (9)	O1-Cu1-O2 ^a	94.25 (8)	02-Ni1-05	89.29 (5)
O3-Mn1-O1 ⁱ	94.95 (3)	O6-Fe1-O1	92.15 (9)	O2-Cu1-O1 ^a	94.25 (8)	02-Ni1-O3	179.31 (4)
O1 ⁱ -Mn1-O3 ⁱ	85.05 (3)	O6-Fe1-O3	173.97 (10)	O2-Cu1-O2 ^a	180.0 (5)	01-Ni1-O4	179.10 (4)
O3-Mn1-O3 ⁱ	180.0 (5)	O5-Fe1-O4	98.64 (9)	O1 ^a -Cu1-O2 ^a	85.75 (8)	01-Ni1-05	88.78 (4)
		O5-Fe1-O2	170.92 (10)			01-Ni1-O3	89.52 (4)
		O5-Fe1-O1	86.46 (9)			04-Ni1-05	91.91 (4)
		O5-Fe1-O3	85.36 (9)			04-Ni1-O3	91.06 (4)
		O4-Fe1-O2	86.64 (9)			O5-Ni1-O3	90.35 (5)
		O4-Fe1-O1	174.88 (9)				
		O4-Fe1-O3	88.40 (9)				
		02-Fe1-01	88.24 (9)				
		O2-Fe1-O3	87.41 (9)				
		01-Fe1-O3	91.60 (9)				



Fig. 3. Molecular structure of complex (3) with an atom numbering scheme common for all reported complexes. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii. Symmetry code (i) -x, 1 - y, 1 - z.



Fig. 4. Molecular structure of complex (4) with an atom numbering scheme common for all reported complexes. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are shown as spheres of arbitrary radii.

complex (4) is neutral, and the central Ni(II) metal ion is coordinated to two anionic pyrazolonato ligands and two neutral methanol ligands. In contrary to complexes (1) and (3), the two pyrazolonato ligands in the complex (4) are in *syn* configuration with respect to the enolato oxygen of the pyrazoline ring (i.e. O2 and O4 as shown in Fig. 4). The geometry around the central metal ion is pseudo-octahedral in which the two pyrazolonato ligands occupy the basal plane, and the two methanol ligands occupy the apical positions. As could also be seen from Table 1, the four basal Ni-O bond lengths are almost equal. Besides, the average C–O bond length on the pyrazolone rings (2.003 Å) is almost equal to the average C–O bond length of the acetyl groups (2.034 Å) which again means that the negative charge is delocalized on the two different oxygen atoms. The other bond lengths and bond angles are in the same range of the previously reported similar structures [35,36].

3.3. Description of the spectroscopic data

The IR spectra of the complexes could be described based on the results of the crystal structures. In the IR spectra of the complexes, the presence of a very intense band at around 1600 cm⁻¹ could be attributed to the stretching vibrations of the carbonyl groups of the acylpyrazolone ligands. As followed from the crystal structures of the complexes, the two C–O groups were almost identical due to the delocalization of the negative charge between the two carbonyl groups, and hence, the C–O bond lengths were between the single and double bonds. The IR spectroscopy also confirms such delocalization. The IR spectra of double bond carbonyl groups are usually observed above 1650 cm⁻¹ and delocalization of negative charge shifts stretching vibration to lower wavenumbers. The observation of the ν (C–O) at around 1600 cm^{-1} is clear evidence of such delocalization. In the IR spectrum of the complex (1), the signal due to the ν (C–O) of the N,Ndimethylformamide ligands were observed at 1649 cm⁻¹ and confirmed the coordination of these ligands. The M-O stretching vibrations were observed at low wavenumbers at around $700 \,\mathrm{cm}^{-1}$. The aromatic and aliphatic ν (C–H) were also observed at around 3000 cm⁻¹. Supplemental Figs. S2–S6 show the IR spectra of the PMAP ligand and complexes (1-4), respectively.

The UV–Vis spectra of the complexes could also be described based on the crystal structural data. In the UV–Vis spectra of the complexes, the very intense bands at around 215 and 250 nm were assigned to the $\pi \rightarrow \pi^*$ transitions. Similar signals were observed for the acylpyrazolone ligand at approximately similar region [21]. The main difference between the UV–Vis spectra of the ligand and the complexes were due to the LMCT which were observed at around 340 nm. The d-d transitions for the complexes (1) and (2) were not observed, even at higher concentrations, most probably due to their very weak absorbances. This behavior is usual for high spin d⁵ complexes. The d-d transitions for complexes (3) and (4) were observed above 600 nm only at higher concentrations. These data are comparable to previously reported similar complexes [28–37]. Besides, the UV–vis spectra of the complexes did not change by time, which means that the complexes were stable in solutions.

3.4. Catalytic studies

The catalytic oxidation of cyclooctene with the four new catalysts gave three products, as shown in Scheme 1. Various reaction conditions, including catalyst type, amount of catalyst, solvent type, solvent amount, reaction time, and oxidant to substrate ratio, were optimized. Fig. 5 summarizes the results for the optimization of different parameter. Table 4 also shows the results of the epoxidation of cyclooctene under optimized conditions for all of the complexes. The optimized reaction time was found to be 24 h and complex (3) with Cu central metal ion was found to be the most efficient catalyst. Then, the amount of the catalyst was optimized, using 10 mmol of cyclooctene, 20 mmol of TBHP, reflux in 10 mL of methanol for 24 h and the optimized amount was found to be 15 μ mol. The catalytic reaction was also performed in 10 mL of different solvents i.e. ethanol, methanol, acetonitrile and chloroform at reflux, in which the complexes were sufficiently soluble. Other reaction conditions were kept constant. The solvent-free



Scheme 1. The products of catalytic epoxidation of cyclooctene with the studied catalysts.



Fig. 5. Results of the optimization of different parameters affecting the epoxidation of cyclooctene by complex (3). The data are the average of four different experiments.

Table 4					
The results of the catalytic	epoxidation	of cyclooctene	with	different	catalysts.

Complex Conversion percent Epoxide selectivity% Other	r products%
(1) 57.8 79.4 20.6 (2) 37.0 81.4 18.6 (3) 84.7 82.8 17.2 (4) 39.1 87.6 12.4	

Conditions: 15μ mol of each catalyst, 10μ mol cyclooctene, 20μ mol TBHP, reflux, 24μ in methanol. The data are the average of four different experiments.

reaction was also done. Methanol was found as the best solvent in which the conversion reached about 85% while with other solvents it was below 50%. The oxidant to substrate ratio was then optimized and 2:1 oxidant:substrate ratio was found as the optimized ratio, keeping

the other reaction conditions as mentioned above.

Based on data in Table 4, the Cu(II) complex with square planar geometry showed the highest catalytic activity while the Fe(III) complex with tris-chelate octahedral structure showed the lowest activity. The lower catalytic activity of Fe(III) complex could be due to the lack of coordination sites available for interaction with the reactants since the highest observed coordination number (CN) for Fe(III) is six. On the other hand and by considering the crystal structures, the Cu(II) complex with square planar geometry and CN = 4 has two available coordination sites for such interactions; hence, it is rational to conclude that the metal ion-reactants interactions are essential. Complexes (1) and (4) with CN = 6 also showed low catalytic activity which confirms the above statement. It follows the previously reported metal ion-oxidant mechanism [38–40]. These findings further confirm that the central metal ion is an important factor in catalytic reactions such as olefin

Table 5

Comparison of the solvent free epoxidation of cyclooctene with TBHP with some recently reported catalysts.

Catalyst	Conversion%	Epoxide selectivity%	Ref
NiL ³	43	77	[44]
NiL ⁴	42	69	[26]
CuL^1	60	64	[45]
CuL ²	85	62	[45]
VOL ¹	56	71	[46]
VOL ³	65	80	[46]
VOL ⁵	66	86	[46]
MoO ₂ L	46	Not reported	[47]
(3)	84.7	82.8	This work

epoxidation [41–43]. Besides, the results of this study further confirm that the Cu(II) complexes could be among the most effective epoxidation catalysts (see Table 5). Fig. S7 shows stepwise monitoring of the reaction products for cyclooctene oxidation with (3) in methanol at optimized conditions obtained at 60 min intervals.

4. Conclusion

Four acylpyrazolone-based transition metal complexes were synthesized and characterized by different spectroscopic techniques, including X-ray crystallography. The catalytic performance of the synthesized complexes was investigated in the epoxidation of cyclooctene to estimate the effect of structural aspects and central metal ion. It was found that the Cu(II) complex showed the highest conversion. High epoxide selectivity was also achieved.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2020.119637.

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