Cyano-Bridged 'Oximato' Complexes: Synthesis, Structure, and Catalase-Like Activities

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The reaction of the 'oximato'-ligand precursor **A** (*Fig. 1*) and metal salts with KCN gave two mononuclear complexes $[ML(CN)(H_2O)_n](ClO_4)$ (**1** and **2**; L = {*N*-(hydroxy-κ*O*)-α-oxo-*N*′-[(pyridin-2-yl-κ*N*)methyl[1,1′-biphenyl]-4-ethanimidamidato-κ*N*′}; M = Co^{II} (**1**), Cu^{II} (**2**); $n = 2$ for Co^{II}, $n = 0$ for Cu^{II}; *Figs. 2* and *3*). The new cyano-bridged pentanuclear 'oximato' complexes $[\{ML(H_2O)_n(NC)\}_4M^1(H_2O)_x](ClO_4)_2$ (**3**–**6**) and trinuclear complexes $[\{ML(H_2O)_n(NC)\}_2M^1L](ClO_4)$ (**7**–**10**) ($[M^1 = Mn^{II}$, Cu^{II}; $x = 2$ for Mn^{II}, $x = 0$ for $Cu^{II}]$) were synthesized from mononuclear complexes and characterized by elemental analyses, magnetic susceptibility, molar conductance, and IR and thermal analysis. The four $[ML(CN)(H_2O)_n]^+$ moieties are connected by a metal(II) ion in the pentanuclear complexe **3**–**6**, each one involving four cyano bridging ligands (*Fig. 4*). The central metal ion displays a square-planar or octahedral geometry, with the cyano bridging ligands forming the equatorial plane. The axial positions are occupied by two aqua ligands in the case of the central Mn-atom. The two $[ML(CN)(H_2O)_n]^+$ moieties and an 'oximato' ligand are connected by a metal(II) ion in the trinuclear complexes **7**–**10**, each one involving two cyano bridging ligands (*Fig. 5*). The central metal ions display a distorted square-pyramidal geometry, with two cyano bridging ligands and the donor atoms of the tridentate 'oximato' ligand. Moreover catalytic activities of the complexes for the disproportionation of hydrogen peroxide (H_2O_2) were also investigated in the presence of 1*H*-imidazole. The synthesized homopolynuclear Cu^{II} complexes **6** and **10** displayed eficiency in disproportion reactions of H_2O_2 producing H_2O and dioxygen thus showing catalase-like activity.

Introduction. – A broad variety of polynuclear metal complexes can be utilized for the design of molecular ferromagnets, as catalysts for many organic reactions, as models of reaction centers of metalloenzymes and DNA binding, and as cleavage reagents, *etc.* [1–6]. Among the variety of methodologies applied to synthesize polynuclear coordination compounds, mononuclear complexes can be used as ligands if they have bridge ligands that can bind the second metal [7–10].

The chemistry of heterobimetallic cyano-bridged complexes has received a strong impulse from the discovery of the Prussian-blue analogs, bridged heteropolymetallic complexes. In these compounds, the linear A–CN–B bridges promote strong ferro- or antiferromagnetic interactions between adjacent metal ions, leading to three-dimensional ferromagnets, antiferromagnets, or ferrimagnets [5][10]. In fact, cyano-bridged metal complexes have been extensively investigated recently; examples of either molecular-based magnetic materials [11–13] or porous metalorganic-material-mimic zeolites [14–16] have been reported. Cyanide represents an optimal ligand to function as terminal as well as bridging ligand, creating an efficient superexchange path when connected by paramagnetic metal centers [17][9]. Paramagnetic entities as bridging moieties allow to build multidimensional structures with a second coordination center, and the resulting complexes demonstrate unique structures and useful magnetic properties [11–13]. Herein we report the preparation, structure characterization, and thermal studies of new mono-, tri-, and pentanuclear Co^{II} and Cu^{II} complexes. In the absence of suitable crystals for X-ray diffraction, molecular-mechanics calculations were performed to give complementary information about probable structures of the ligand and the mononuclear complexes.

In normal mammalian cells, reactive oxygen species (ROS) are produced through metabolic reactions resulting from aerobic respiration. Low levels of ROS are essential for proper cell function, and a fine balance exists between the level of ROS produced during normal cellular metabolism and the amount of endogenous antioxidants (such as ROS scavengers and enzymes) present in the cells which protect tissues from oxidative damage [18][19]. Recently, it has been found that ROS such as the superoxide radical or H_2O_2 are important regulators of cell death. Particularly, H_2O_2 is implicated as a mediator of apoptosis in cells [19–21]. Catalase enzymes are important antioxidant metalloenzymes that catalyze the decomposition of H_2O_2 to H_2O and dioxygen. Thus, they protect cells from the toxic effects of H_2O_2, the latter being linked to a variety of pathological consequences such as aging, diabetes, and cancer [22][23].

A number of Mn-containing catalases have been isolated and characterized [24–27]. The direct utilization of these natural enzymes as pharmaceutical agents is limited because of low membrane permeability as a consequence of their high molecular mass. So considerable efforts were made to obtain nontoxic, low-molecular-mass biomimetic molecules, which are able to destroy the forming H_2O_2. Compared with Mn-containing model systems [26][27], the reported Cu-containing systems are relatively rare [19][28–30]. In this study, catalase-mimicking activity for the disproportionation of H_2O_2 of the synthesized coordination compounds are also investigated.

Results and Discussion. – *Syntheses and Some Properties of Complexes* **1**–**10**. The condensation of *N*-hydroxy-α-oxo[1,1′-biphenyl]-4-ethanimidoyl chloride with pyridine-2-methanamine gave the ligand precursor *N*-hydroxy-α-oxo-*N′*-(pyridin-2-ylmethyl)[1,1′-biphenyl]-4-ethanimidamide[1]) (**A**) (*cf. Fig. 1*) [31]. Complexes including cyano ligands were synthesized by a modified literature method [10]; mononuclear metal(II) complexes are useful starting materials for the synthesis of homo- and heteropolynuclear complexes with interesting magnetic properties [10][32][33]. The modeled molecular structures of ligand precursor **A** and the mononuclear complexes **1** and **2** are shown on *Figs. 1–3*, respectively. In these complexes, the metal(II) ions are bound by the pyridine and methanamine N-atoms and the 'oximato' O-atom. In the pentanuclear complexes **3**–**6**, the four mononuclear complex moieties are connected by a Mn^{II} or Cu^{II} central atom *via* four cyano bridging ligands (*Fig. 4*). The Mn^{II} ions display a distorted octahedral geometry, with the cyano ligands forming the equatorial plane and the axial positions being occupied by two aqua ligands. In the trinuclear complexes **7**–**10** (*Fig. 5*), the two mononuclear complex moieties are connected by a

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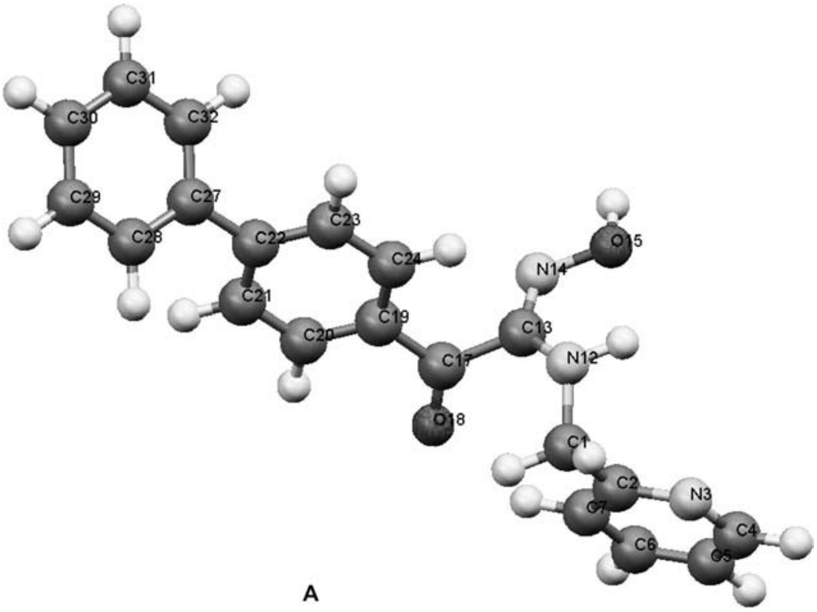
[1]) Ligand-precursor name of the preferred tautomer (*cf. Chem. Abstr.*).

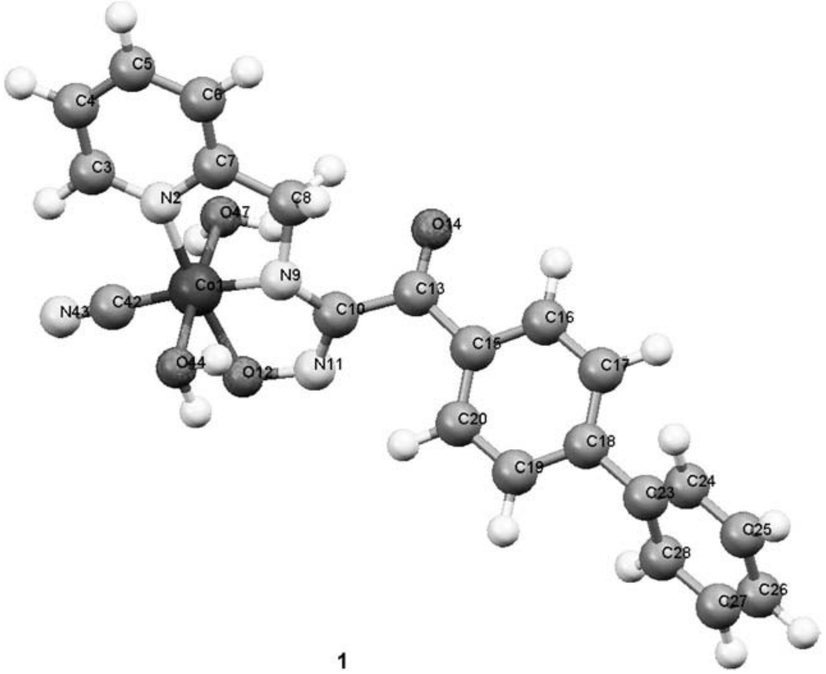
mononuclear Mn^{II} or Cu^{II} complex moiety *via* two cyano bridging ligands. The Mn^{II} or Cu^{II} ions display a distorted square-pyramidal geometry. The complexes **1**–**10** are insoluble in H_2O and common organic solvents but show maximum solubility in DMF and DMSO at room temperature. Attempts to isolate crystals suitable for X-ray diffraction were unsuccessful. Therefore, the general formula of the complexes is ascertained by elemental analyses and IR and thermogravimetric-analysis (TGA) data. The molar-conductance values of the mononuclear complexes **1** and **2** were 22 and 36 $\Omega^{-1}cm^2mol^{-1}$, respectively, which indicated their nonionic nature [34–36]. The pentanuclear complexes **3**–**6** and trinuclear complexes **7**–**10** behaved as ionic compounds which gave molar-conductance values of 135–174 and 78–109 $\Omega^{-1}cm^2mol^{-1}$, respectively. These values indicated that the polynuclear complexes containing perchlorate ions behaved as 1:2 (**3**–**6**) [4] and 1:1 (**7**–**10**) [37] electrolytes consistent with the formulae from the elemental analyses. From all of the above observations, the proposed structures of the pentanuclear and trinuclear complexes **3**–**6** and **7**–**10**, respectively, were confirmed (*Figs. 4* and *5*).



A

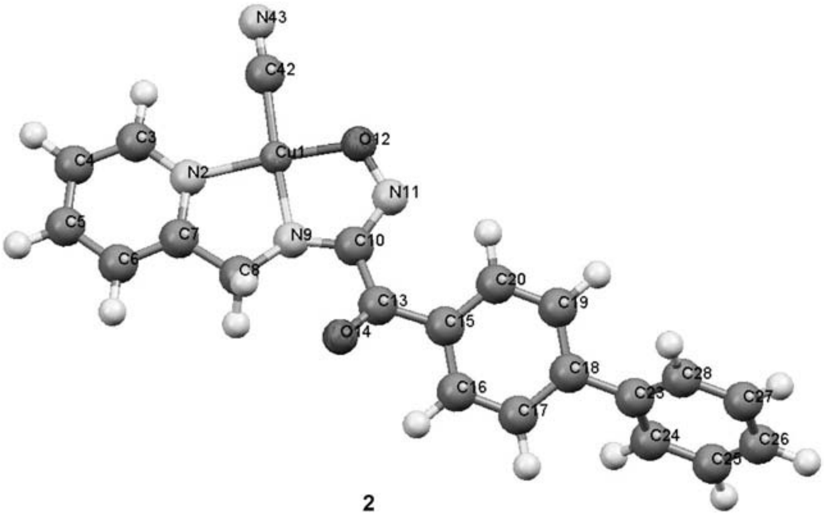
Fig. 1. *MOPAC(PM6)-Optimized structure of the ligand precursor* N*-hydroxy-α-oxo-*N′*-(pyridin-2-ylmethyl)[1,1′-biphenyl]-4-ethanimidamide*[1]) (**A**)

IR Spectra. The IR spectra of the ligand precursor **A** and its complexes exhibited various bands in the 400–4000 cm^{-1} region. The IR-active bands were in the region 3418–3444 cm^{-1} for complexes with characteristics of $\tilde{\nu}$(N–H). For the $\tilde{\nu}$(C≡N) mode of the complexes, two main band systems of comparable intensity were observed. The band at 2162 cm^{-1} for **1** and at 2131 cm^{-1} for **2** were assigned to terminal C≡N stretching, and the other bands at *ca.* 2141–2181 cm^{-1} for the polynuclear complexes **3**–**10** were assigned to the intermetallic C≡N stretching mode [5][33]. The polynuclear complexes **3**–**10** showed medium bands near 1160–1180 cm^{-1} and weak



1

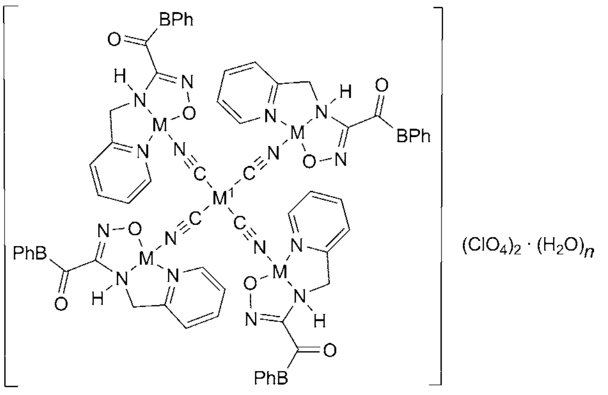
Fig. 2. *MOPAC(PM6)-Optimized structure of the mononuclear* Co^{II} *complex* **1**



2

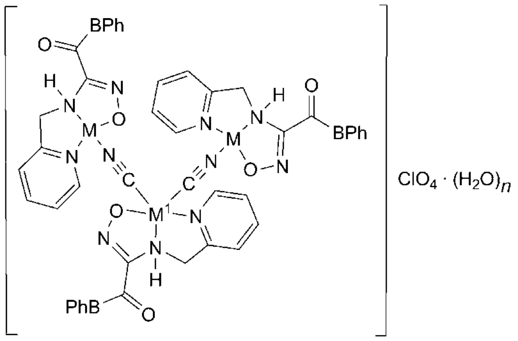
Fig. 3. *MOPAC(PM6)-Optimized structure of the mononuclear* Cu^{II} *complex* **2**

bands at 1028 – 1098 cm^{-1}, indicating the presence of uncoordinated perchlorate anion [4][38]. All the other peaks appeared at their usual positions; only slight differences between the complexes were observed.



3 – 6

Fig. 4. *Pentanuclear complexes* **3**–**6** *of* N-*hydroxy-α-oxo-*N'-*(pyridin-2-ylmethyl)[1,1'-biphenyl]-4-ethanimidamidato*[1]) (M = Cu^{II}, Co^{II}; M^1 = Cu^{II}, Mn^{II}; BPh = [1,'-biphenyl]-4-yl; $(H_2O)_n$ means aqua ligands, *cf. Exper. Part*).



7 – 10

Fig. 5. *Trinuclear complexes* **7**–**10** *of* N-*hydroxy-α-oxo-*N'-*(pyridin-2-ylmethyl)[1,1'-biphenyl]-4-ethanimidamidato*[1]) (M = Cu^{II}, Co^{II}; M^1 = Cu^{II}, Mn^{II}; BPh = [1,1'-biphenyl]-4-yl; $(H_2O)_n$ means aqua ligands, *cf. Exper. Part.*)

Magnetic Studies. The room-temperature magnetic moments of the complexes **1**–**10** showed that they all were paramagnetic. The measured magnetic moments of the mononuclear Co^{II} and Cu^{II} complexes **1** and **2** were 1.30 and 1.26 B.M., respectively. This values are in aggreement with a spin value of 1.73 μ_B for low-spin octahedral Co^{II} and square-planar Cu^{II} complexes [39].

The very complicated magnetic behavior of the heteropolynuclear complexes **3**–**10** concerns the exchange interaction between the paramagnetic centers. The nearest-neighbor transition metal ions in these complexes were linked by a bridging ligand. One of the important bridging ligands in the chemistry of heteropolynuclear complexes is the cyano ligand, which has been widely used as a linker to prepare magnetic molecules. Resulting in such a large metal–metal distance, it is reasonable to neglect direct metal–metal interactions; the cyano linkage provides an efficient pathway for a superexchange between metal ions [40][41], *i.e.*, an interaction through the bridging ligand must be operative. Recently, *Entley* and *Girolami* [42] argued that mainly the cyano π^* antibonding orbitals were responsible for the exchange interaction [40].

The magnetic moments of the pentanuclear complexes **3**–**6** amounted to 0.61–4.43 B.M., and the magnetic moments of the trinuclear complexes **7**–**10** were 0.53–1.99 B.M. The antiferromagnetic interaction was supported by the fact that the magnetic-susceptibility values were well below that expected for the total spin-only value of metal(II) ions of polynuclear complexes. Some bridge ligands generally mediate very strong antiferromagnetic exchange interactions between d^9 Cu^{II} centers [31][43–45] and the other heteronuclear centers [10][32][41][46], as reported previously for polynuclear bridged complexes.

Thermal Analyses. The thermal behavior of some of the prepared complexes is summarized in *Table 1.* The mononuclear Cu^{II} complex **2** was decomposed in two steps. A biphenyl group of the ligand and one C≡N group (theoretical mass loss of 37.88 and 6.44%, resp.) could be eliminated in the temperature range 40–493° with a mass loss of 38.61 and 6.86%. The complex showed residues not conforming to the corresponding metallic residue such as metal oxides or metallic Cu, even at 900°, indicating that the decomposition of the organic moiety remained incomplete even at this temperature.

Table 1. *Thermoanalytical Results* thermogravimetry (TG) and differential thermogravimetry (DTG) *of Metal Complexes*

	TG range [°]	T_{max} (DTG) [°]	Exper. mass loss (calc.) [%]	Assignment	Metallic residue
2	30–493	356, 437	38.61 (37.88)	loss of biphenyl group	decomposition in progress
	486–493	493	6.86 (6.44)	loss of CN group	
5	30–259	167	12.78 (12.14)	loss of 2 H_2O molecules and 2 ClO_4	decomposition in progress
	259–723	300, 413	31.46 (31.65)	loss of biphenyl groups	
6	30–253	173	10.73 (10.45)	loss of ClO_4 groups	decomposition in progress
	253–680	273, 344, 403, 470	32.17 (31.51)	loss of biphenyl groups	
10	30–200	193	7.15 (7.61)	loss of ClO_4 group	decomposition in progress
	200–500	292	34.32 (34.42)	loss of biphenyl groups	

Also the pentanuclear Cu_4Mn complex **5** was thermally decomposed in two steps. The first step within the temperature range 30–259° (T_{max} (DTG) 167°) may be attributed to the loss of two coordinated H_2O molecules and ClO_4 groups. The second step occurred within the temperature range 259–723°. Above 259° the complex decomposed in a gradual manner rather than by a sharp decomposition, which was attributed to fragmentation and thermal degradation of the organic moiety. The complex showed residues not conforming to the corresponding metallic residue, even at 900°, indicating that the decomposition of the organic moiety remained incomplete even at this temperature.

The pentanuclear Cu_5 complex **6** was thermally decomposed in two steps. The first step within the temperature range 30–253° (T_{max} (DTG) 173°) may be attributed to the loss of ClO_4 groups. The second step within the temperature range 253–680° were due to the liberation of biphenyl groups of the ligands. The complex showed residues not conforming to the corresponding metallic residue, even at 900°, indicating that the decomposition of the organic moiety remained incomplete even at this temperature.

The trinuclear Cu complex **10** exhibited the first mass loss in the temperature range 30–200°, with an T_{max} (DTG) at 193°, which may be attributed to the liberation of the ClO_4 group. The other decomposition step within the temperature range 200–500°, with a T_{max} (DTG) at 292°, were due to the liberation of bihenyl groups of the ligands. But the decomposition of the complex remained incomplete even at 900°.

Molecular Modeling. Since no single crystals suitable for X-ray determination could be isolated, structural information for the ligand precursor **A** and its mononuclear Cu^{II} and Co^{II} complexes **1** and **2** were obtained by molecular-modelling techniques. Thus, the lowest-energy model structures of **A**, **1**, and **2** were determined, revealing the possible arrangement of the ligand around the metals. The molecular structures of these compounds determined by the experimental spectroscopic, conductivity, and magnetic studies (see above) were in agreement with these calculated theoretic of structural data. The optimized structure of ligand precursor **A** is shown in *Fig. 1* (see above), and the bond angles and bond lengths are given in *Supplementary Material S.1* and *S.2*[2]).

The tridentate ligand derived from **A** forms, together with two aqua and one cyano ligand, an octahedral complex **1** with Co^{II}, and, together with one cyano ligand a square-planar complex **2** with Cu^{II} where the fourth site is occupied by the cyano ligand. In the octahedral Co complex **1**, the Co^{II} ion is nearly in the mean plane of the four coordinating atoms N, N, O, and C of the organic and cyano ligands (0.01 Å off the plane). The Co–N bond distances of 1.88 Å and the equatorial Co–O distance of 1.93 Å are comparable to literature values (Co^{II}–N 2.09 and Co^{II}–O 2.05 Å (Δ *ca.* 0.2 Å) [47]. The Co–C distance of 1.87 Å and C≡N distance of 1.16 Å are close to the known experimental values 1.88 and 1.13 Å [48]. The N ··· N bite distance is 2.60 Å and the N ··· O bite distance 2.57 Å. The axial sites are occupied by two H_2O molecules, the Co–O (H_2O) bond distances being 2.01 and 2.07 Å comparable to the literature value of 2.16 Å [47]. The two benzene rings of the organic ligand are skewed at an angle of 56.4° to each other. The optimized structure of the mononuclear Co^{II} complex **1** is given in *Fig. 2* (see above), and the calculated bond lengths and bond angles are given in *Supplementary Material S.3* and *S.4*[2]).

In the Cu complex **2**, the Cu^{II} ion is nearly on the mean plane of the four coordinating atoms N, N, O, and C of the organic and cyano ligands (0.06 Å off the plane). The Cu–N distances are 1.91 and 1.80 Å and the Cu–O distance is 1.78 Å. These values are close to the values found in the literature (Cu^{II}–N 1.92 and 1.94 Å and Cu^{II}–O 1.90 Å) [49]. The Cu–C distance is 1.84 Å, and the C≡N distance 1.15 Å, close to the known experimental values 1.94 and 1.16 Å [50]. The N ··· N bite distance is 2.56 Å, and the N ··· O bite distance 2.48 Å. The two benzene rings of the organic ligand are skewed at an angle of 57.6° to each other. The optimized structure of the mononuclear Cu^{II} complex **2** is given in *Fig. 3* (see above), and the calculated bond lengths and bond angles are given in *Supplementary Material S.5* and *S.6*[2]).

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[2]) Electronic *Supplementary Material* is available upon request from the senior autor (*F. K.*).

Catalase-Like Activity. The catalase mimetic properties of the ligand precursor **A** and its complexes **1**–**10** in the presence of the base 1*H*-imidazole were investigated by measuring the volume of evolved O-atom (O_2) from hydrogen peroxide (H_2O) during the course of the reaction. The results from these reactions are summarized in *Table 2* and *Fig. 6*. It should be noted that none of the complexes exhibited efficient catalytic activity on its own, and the 1*H*-imidazole base itself caused only a very slight disproportionation of H_2O_2, this reaction was greatly enhanced when the complexes were included in the reaction mixture with the base. Such an enhancement in the presence of added base has also been reported by other researchers [51–56]. It was suggested that the heterocyclic bases (pyridine and 1*H*-imidazole, *i.e.*, strong π-donors) may be essential in the catalytic disproportionation of H_2O_2 by catalase since they are known to be present in the vicinity of the active site of catalase and other manganoenzymes [57]. In addition, the significant acceleration of the decomposition of H_2O_2 upon addition of 1*H*-imidazole revealed a significant push effect. Such a push effect has been prominent in proposed mechanisms for dioxygen activation by heme enzymes (and by their synthetic analog) and emphasizes the role that the proximal axial ligand can play in promoting O–O bond cleavage. In these mechanisms, the heterocyclic base accepts an H-atom from the O-atom of H_2O_2 that binds to the central atom and transfers it to the other O-atom to generate a good leaving group. Thus, heterolytic O–O bond cleavage is achieved [58][59].

Table 2 illustrates the rate of disproportionation of H_2O_2 by the evolution of O_2 from the respective reactions for the complexes over the first 20 min. All the complexes

Table 2. *Time Course of O_2 Evolution from H_2O_2, Disproportionated by the Ligand Precursor* **A** (1 mol-equiv.) *and Its Complexes* **1**–**10** (1 mol-equiv.) *with Added 1*H*-Imidazole* (im; 50 mg) *at 25°*

Time [min]	Amount of disproportionated H_2O_2 molecules [mol-equiv.]											
	im	**A**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	24	38	38	76	41	39	126	173	49	69	85	205
2	28	39	44	96	49	58	195	351	55	104	153	299
3	34		49	110	55	72	225	362	60	134	197	315
4	36		55	118	65	82	236		71	150	221	323
5			66	126	71	91	241		82	159	238	331
6			90	132	79	99			91	162	259	
7			106	137	88	104			102		257	
8			123	148	99	107			113		274	
9			129	153	106	117			118		276	
10					113	120			118		288	
11					120	131			120			
12					123	132						
13					128							
14					134							
15					142							
16					143							
17					147							
18					150							
19					158							

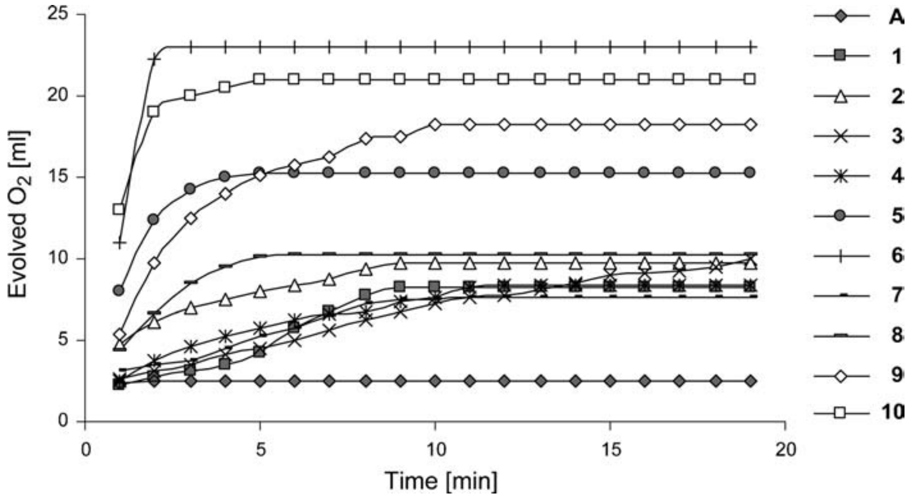

Fig. 6. *Time courses of dioxygen evolution in the disproportionation of H_2O_2 by the ligand precursor* (**A**) *and its complexes* **1**–**10** *in DMF* ([complex] = 0.005 mmol, [H_2O_2] = 2.60 mmol, 298 K)

showed catalytic decomposition of H_2O_2 in the presence of 1*H*-imidazole. Over the first minute, complex **10** (1 mol-equiv.) appeared to be the most efficient catalyst with 205 mol-equiv. of H_2O_2 disproportionated *i.e.*, the turnover number (ton) was 205. Comparing these results with previously published tons [56], the catalase activity of complexes **6** and **10** was similar to that of some dinuclear Mn^{III} complexes (ton 160–280). The ligand precursor **A** and complex **1** appeared to be the least efficient catalyst over the first minute with 1 mol-equiv. of **A** or **1** knocking down just 38 mol-equiv. of H_2O_2. But, comparison of the total number of mol-equiv. of H_2O_2 disproportionated by 1 mol-equiv. of complex showed that complex **6** was the most effective catalyst (362 mol-equiv. of H_2O_2). The time course of the O_2 evolution is shown in *Fig. 6*. The H_2O_2-disproportionation efficiency of the complexes in the presence 1*H*-imidazole followed the order: **6** > **10** > **9** > **5** > **8** > **3**. The ligand precursor **A** and the other complexes **1**, **2**, **4**, and **6** were less effective for the catalytic decomposition compared to the other synthesized complexes. Thus, as a result of these catalase-like activity studies, the penta- and trihomonuclear Cu^{II} complexes **6** and **10** were found to exhibit a high H_2O_2 disproportionation efficiency when compared to the other synthesized complexes.

Conclusions. – In this work, we described the pentanuclear and trinuclear hetero- and homo-metallic complexes **3**–**10** obtained from mononuclear [Co^{II} ('oximato')] and [Cu^{II} ('oximato')] complexes **1** and **2**, respectively, and these complexes were characterized by elemental analyses, spectral, magnetic, and conductance measurements, and thermal and theoretical methods. In addition, we tested the catalytic activity of the complexes toward the disproportionation of H_2O_2. The catalytic results indicated that homopolynuclear Cu^{II} complexes exhibited good catalase activity and may be suitable and functional as a model for the pseudocatalase enzyme.

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Experimental Part

General. The 'oximato' ligand precursor **A** was synthesized according to a procedure described previously [31]. All solvents, metal salts, and other chemicals used for the synthesis and physical measurements were purchased from *Aldrich*, *J. T. Baker*, and *Merck* and used as received. IR Spectra (4000 – 400 cm^{-1}): *Shimadzu-IRPrestige-21* FT-IR spectrophotometer; KBr pellets; in cm^{-1}. Molar conductance: *Optic-Ivymen* conductivity meter; freshly prepared 10^{-3} M dimethylformamide (DMF) soln. at r.t.; Λ_M in Ω^{-1} cm^2 mol^{-1}. Magnetic susceptibility: *Sherwood-Scientific-MX1* magnetic-susceptibility balance at r.t.; μ_{eff} in B.M. Thermogravimetric analyses: *Perkin-Elmer-Diamond* thermal analyzer; the experiments were carried out in a dynamic N_2 atmosphere (20 ml min^{-1}) with a heating rate of 10° min^{-1} in the temp. range 20 – 900°. Elemental analyses: *Leco-932-CHNS* analyzer; (C, H, and N); *Perkin-Elmer-Optima-5300-DV-ICP-OES* spectrometer (Mn, Co, and Cu).

Computational Details. The structures of **A** and its mononuclear complexes **1** and **2** were modeled by the MOPAC 2007 [60] program by using the PM6 method [61]. Selected parts of the molecules not containing the metal ion were preoptimized by molecular-mechanics methods. Several cycles of energy minimization had to be carried out for the molecules. The geometries were optimized with Eigen Vector. The optimized structures had a root-mean-square gradient of less than one, and a self-consistent field was achieved.

Studies on the Catalase-Like Activity. The catalytic activity of **A** and its complexes **1** – **10** towards the disproportionation of H_2O_2 was investigated by measuring the volume of evolved O_2 during the course of the reaction: A 50-ml three-necked round-bottom flask (burette and two rubber septa) containing a suspension of the complex (0.005 mmol solid sample) in DMF (10 ml) was placed in a water bath (25°). While the suspension was stirred, H_2O_2 (2.60 mmol, 0.150 ml) was injected into it through the rubber septum by a microsyringe. Volumes of evolved O_2 were measured at 1-min time intervals by volumometry. In cases where 1*H*-imidazole (50 mg) was added, this was introduced into the reaction vessel before the addition of H_2O_2 (in the absence of the 1*H*-imidazole, the complexes were either inactive or very weak catalysts for this reaction).

Caution. Perchlorate salts of metal complexes are potentially explosive, and cyanides are very toxic. Thus, these starting materials should be handled in small quantities and with great caution.

Mononuclear Complexes **1** *and* **2**. The mononuclear complexes were synthesized by the modification of a literature method [10]: A soln. of ligand precursor *N*-hydroxy-*α*-oxo-*N'*-(pyridin-2-ylmethyl)[1,1'-biphenyl]-4-ethanimidamide1) (**A**; 0.68 g, 2.02 mmol) in MeOH (10 ml) was mixed with an aq. soln. (5 ml) of metal(II) perchlorate hexahydrate (2.0 mmol; 0.73 g of $Co(ClO_4)_2 \cdot 6\,H_2O$ or 0.74 g of $Cu(ClO_4)_2 \cdot 6\,H_2O$) with stirring. A soln. of KCN (1.30 g, 2.0 mmol) in H_2O (10 ml) was added to the above soln. and the resulting mixture was stirred for 2 h. The precipitate was filtered off, washed with EtOH and H_2O, and dried (P_2O_5).

*Diaqua(cyano-κ*C*)[*N*-(hydroxy-κ*O*)-α-oxo-*N'*-[(pyridin-2-yl)κ*N*)methyl][1,1'-biphenyl]-4-ethanimidamidato-κ*N*}cobalt* ([CoL(CN)(H_2O)$_2$]; **1**): Brown solid. Yield 98%. M.p. 142° (dec.). FT-IR (KBr): 3424 (br., NH), 2162*s* (C≡N), 1604*s* (C=O), 1559*m* (C=N), 978*m* (NO). Λ_M: 22. μ_{eff} = 1.30. Anal. calc. for $C_{21}H_{20}CoN_4O_3$: C 57.94, H 4.63, Co 13.54, N 12.87; found: C 57.75, H 4.43, Co 13.52, N 12.59.

*(Cyano-κ*C*)[*N*-(hydroxy-κ*O*)-α-oxo-*N'*-[(pyridin-2-yl)κ*N*)methyl][1,1'-biphenyl]-4-ethanimidamidato-κ*N*}copper* ([CuL(CN)]; **2**): Light brown solid. Yield 99%. M.p. 139° (dec.). FT-IR (KBr): 3418 (br., NH), 2131*s* (C≡N), 1658*s* (C=O), 1603*m* (C=N), 985*m* (NO). Λ_M: 36. μ_{eff} = 1.26. Anal. calc. for $C_{21}H_{16}CuN_4O$: C 62.45, H 3.99, Cu 15.73, N 13.87; found: C 62.14, H 3.71, Cu 15.28, N 13.97.

Pentanuclear Complexes **3** – **6**. The pentanuclear complexes were prepared similarly to the procedure reported in [10]: To a soln. of mononuclear complex **1** or **2** (0.4 mmol; 0.17 g of **1** or 0.16 g of **2**) in MeOH (10 ml) was added dropwise a soln. of $Mn(ClO_4)_2 \cdot 6\,H_2O$ (0.1 mmol, 0.035 g) or $Cu(ClO_4)_2 \cdot 6\,H_2O$ (0.1 mmol, 0.037 g) in H_2O (5 ml). The mixture was stirred and heated to reflux for 16 h and then allowed to reach r.t. The solid product was filtered off, washed with cold EtOH and Et_2O, dried and kept in a desiccator over P_4O_{10}.

Diaquatetrakis[μ-(cyano-κC:κN)]tetrakis{diaqua[N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}cobalt}manganese Perchlorate (1:2) ($[\{CoL(H_2O)_2NC)\}_4Mn(H_2O)_2](ClO_4)_2$; **3**): Brown solid. Yield 28.27%. M.p. 97° (dec.). FT-IR (KBr): 3434 (br., NH), 2181*s* (C≡N), 1609*s* (C=O), 1559*m* (C=N), 1164*m* and 1059*w* (ClO_4), 982*m* (NO). Λ_M: 174. $\mu_{eff} = 3.17$. Anal. calc. for $C_{84}H_{84}Cl_2Co4\ MnN_{16}O_{26}$: C 48.15, H 3.89, Co 11.25, Mn 2.62, N 10.83; found: C 48.12, H 3.72, Co 11.21, Mn 2.74, N 10.55.

Octaaqua(coppertetrakis[μ-(cyano-κC:κN)]tetrakis{N-hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}tetracobalt Perchlorate (1:2) ($[\{CoL(H_2O)_2NC)\}_4Cu](ClO_4)_2$; **4**): Brown solid. Yield 27.60%. M.p. 104° (dec.). FT-IR (KBr): 3444 (*br.*, NH), 2181*s* (C≡N), 1604*s* (C=O), 1554*m* (C=N), 1160*m* and 1036*w* (ClO_4), 974*m* (NO). Λ_M: 135. $\mu_{eff} = 4.43$. Anal. calc. for $C_{84}H_{80}Cl_2Co_4CuN_{16}O_{24}$: C 48.79, H 3.89, Co 11.40, Cu 3.07, N 10.83; found: C 48.68, H 3.60, Co 11.55, Cu 3.32, N 10.49.

Diaquatetrakis[μ-(cyano-κC:κN)]tetrakis{{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}copper}manganese Perchlorate (1:2) ($[\{CuL(NC)\}_4Mn(H_2O)_2](ClO_4)_2$; **5**): Green-brown solid. Yield 36.27%. M.p. 196°. FT-IR (KBr): 3444 (br., NH), 2141*s* (C≡N), 1651*s* (C=O), 1604*m* (C=N), 1176*m* and 1051*w* (ClO_4), 982*m* (NO). Λ_M: 152. $\mu_{eff} = 0.61$. Anal. calc. for $C_{84}H_{68}Cl_2Cu_4MnN_{16}O_{18}$: C 51.23, H 3.47, Cu 12.91, Mn 2.78, N 11.37; found: C 51.05, H 3.24, Cu 12.75, Mn 2.80, N 11.18.

Tetrakis[μ-(cyano-κC:κN)]tetrakis{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}pentacopper Perchlorate (1:2) ($[\{CuL(NC)\}_4Cu](ClO_4)_2$; **6**): Brown solid. Yield 35.23%. M.p. 177° (dec.). FT-IR (KBr): 3424 (br., NH), 2141*s* (C≡N), 1659*s* (C=O), 1604*m* (C=N), 1180*m* and 1028*w* (ClO_4), 982*m* (NO). Λ_M: 141. $\mu_{eff} = 0.88$ Anal. calc. for $C_{84}H_{64}Cl_2Cu_5N_{16}O_{16}$: C 51.95, H 3.32, Cu 16.36, N 11.54; found: C 51.67, H 3.22, Cu 16.18, N 11.53.

Trinuclear Complexes **7**–**10**. The trinuclear complexes were prepared similarly to the procedure reported in [10]: A soln. of (0.033 g, 0.10 mmol) was added to a soln. of **1** (0.079 g, 0.20 mmol) or **2** (0.080 g, 0.20 mmol) in MeOH (10 ml). To this mixtures was added dropwise a soln. of 0.10 mmol of metal salt (0.035 g of $Mn(ClO_4)_2 \cdot 6\ H_2O$ or 0.037 g of $Cu(ClO_4)_2 \cdot 6\ H_2O$) in H_2O (5 ml). The mixture was stirred and heated under reflux for 12 h and then allowed to reach r.t. The solid product was filtered, washed with cold EtOH and then with cold Et_2O, dried and kept, in a desiccator over P_4O_{10}.

Bis[μ-(cyano-κC:κN)]bis{diaqua{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}cobalt}{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}manganese Perchlorate (1:1) ($[\{CoL(H_2O)_2(NC)\}_2(MnL)](ClO_4)$; **7**): Brown solid. Yield: 34.85%. M.p. 205°. FT-IR (KBr): 3424 (br., NH), 2171*s* (C≡N), 1609*s* (C=O), 1559*m* (C=N), 1164*m* and 1098*w* (ClO_4), 974*m* (NO). Λ_M: 92. $\mu_{eff} = 1.99$. Anal. calc. for $C_{62}H_{56}ClCo_2MnN_{11}O_{14}$: C 53.67, H 4.06, Co 8.50, Mn 3.96, N 11.10; found: C 53.55, H 4.25, Co 8.73, Mn 3.70, N 11.49.

Tetraaquabis[μ-(cyano-κC:κN)]bis{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}{{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}copper}dicobalt Perchlorate (1:1) ($[\{CoL(H_2O)_2(NC)\}_2(CuL)](ClO_4)$; **8**): Brown solid. Yield 16.82%. M.p. 141° (dec.). FT-IR (KBr): 3434 (br., NH), 2171*s* (C≡N), 1604*s* (C=O), 1559*m* (C=N), 1160*m* and 1059*w* (ClO_4), 974*m* (NO). Λ_M: 109. $\mu_{eff} = 1.38$. Anal. calc. for $C_{62}H_{56}ClCo_2CuN_{11}O_{14}$: C 53.34, H 4.04, Co 8.44, Cu 4.55, N 11.03; found: C 53.57, H 4.10, Co 8.64, Cu 4.70, N 11.30.

Bis[μ-(cyano-κC:κN)]{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}bis{{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}copper}manganese Perchlorate (1:1) ($[\{CuL(NC)\}_2(MnL)](ClO_4)$; **9**): Green-brown solid. Yield 21.97%. M.p. 168°. FT-IR (KBr): 3434 (br., NH), 2141*s* (C≡N), 1655*s* (C=O), 1599*m* (C=N), 1172*m* and 1055*w* (ClO_4), 974*m* (NO). Λ_M: 78. $\mu_{eff} = 0.53$. Anal. calc. for $C_{62}H_{48}ClCu_2MnN_{11}O_{10}$: C 56.22, H 3.65, Cu 9.59, Mn 4.14, N 11.63; found: C 56.52, H 3.75, Cu 9.56, Mn 4.12, N 11.96.

Bis[μ-(cyano-κC:κN)]tris{N-(hydroxy-κO)-α-oxo-N′-[(pyridin-2-yl-κN)methyl][1,1′-biphenyl]-4-ethanimidamidato-κN′}tricopper Perchlorate (1:1) ($[\{CuL(NC)\}_2(CuL)](ClO_4)$; **10**): Brown solid. Yield

23.30%. M.p. 195° (dec.). FT-IR (KBr): 3424 (br., NH), 2141*s* (C≡N), 1656*s* (C=O), 1604*m* (C=N), 1180*m* and 1032*w* (ClO_4), 978*m* (NO). Λ_M: 86. $\mu_{eff} = 0.70$ Anal. calc. for $C_{62}H_{48}ClCu_3N_{11}O_{10}$: C 55.86, H 3.63, Cu 14.30, N 11.56; found: C 55.43, H 3.40, Cu 14.75, N 11.8.

Supplementary Material. The optimized structure of the ligand precursor **A** and the mononuclear complexes **1** and **2**, calculated by the MOPAC 2007 program and the PM6 method, bond angles, and bond lengths are available on request[2]).

REFERENCES

[1] H.-C. Wu, P. Thanasekaran, C.-H. Tsai, J.-Y. Wu, S.-M. Huang, Y.-S. Wen, K.-L. Lu, *Inorg. Chem.* **2006**, *45*, 295.

[2] C. Maxim, T. D. Pasatoiu, V. C. Kravtsov, S. Shova, C. A. Muryn, R. E. P. Winpenny, F. Tuna, M. Andruh, *Inorg. Chim. Acta* **2008**, *361*, 3903.

[3] S. Anbu, M. Kandaswamy, P. Suthakaran, V. Murugan, B. Varghese, *J. Inorg. Biochem.* **2009**, *103*, 401.

[4] B. Dede, I. Özmen, F. Karipcin, M. Cengiz, *Appl. Organomet. Chem.* **2009**, *23*, 512.

[5] M. Fenbinteanu, S. Tanase, M. Andruh, Y. Journaux, F. Cimpoesu, I. Strenger, E. Rivière, *Polyhedron* **1999**, *18*, 3019.

[6] D. Luneau, 'Molecular Magnets', in 'Current Opinion in Solid State and Materials Science', Vol. 5, p. 123, Pergamon Press, Oxford, U.K. **2001**.

[7] S. Ohkoshi, K. Hashimoto, *J. Photochem. Photobiol., C* **2001**, *2*, 71.

[8] R. Lescouëzec, L. M. Toma, J. Vaissermann, M. Verdaguer, F. S. Delgado, C. Ruiz-Pérez, F. Lloret, M. Julve, *Coord. Chem. Rev.* **2005**, *249*, 2691.

[9] D. Ghoshal, A. K. Ghosh, T. K. Maji, J. Ribas, G. Mostafa, E. Zangrando, N. R. Chaudhuri, *Inorg. Chim. Acta* **2006**, *359*, 593.

[10] J.-Z. Gu, H.-Z. Kou, L. Jiang, T.-B. Lu, M.-Y. Tan, *Inorg. Chim. Acta* **2006**, *359*, 2015.

[11] Z. J. Zhong, H. Seino, Y. Mizobe, M. Hidai, A. Fujishima, S. Ohkoshi, K. Hashimoto, *J. Am. Chem. Soc.* **2000**, *122*, 2952.

[12] E. Coronado, C. J. Gómez-García, A. Nuez, F. M. Romero, E. Rusanov, H. Stoeckli-Evans, *Inorg. Chem.* **2002**, *41*, 4615.

[13] H.-R. Wen, Y.-Z. Tang, C.-M. Liu, J.-L. Chen, C.-L. Yu, *Inorg. Chem.* **2009**, *48*, 10177.

[14] M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391.

[15] F. Tuna, S. Golhen, L. Ouahab, J.-P. Sutter, *C. R. Chim.* **2003**, *6*, 377.

[16] K. L. Gurunatha, G. Mostafa, D. Ghoshal, T. K. Maji, *Cryst. Growth Des.* **2010**, *10*, 2483.

[17] O. Kahn, *Nature (London, U.K.)* **1995**, *378*, 667.

[18] 'Oxidative Stress and the Molecular Biology of Antioxidant Defenses', Ed. J. D. Scandalis, Cold Spring Harbor Laboratory Press, Raleigh, USA, 1997.

[19] M. Devereux, D. O'Shea, M. O'Connor, H. Grehan, G. Connor, M. McCann, G. Rosair, F. Lyng, A. Kellett, M. Walsh, D. Egan, B. Thati, *Polyhedron* **2007**, *26*, 4073.

[20] **S. M.** Cardoso, C. Pereira, C. R. Oliveira, *Biochem. Biophys. Res. Commun.* **1998**, *246*, 703.

[21] M. Matés, *Toxicology* **2000**, *153*, 83.

[22] M. Zámocký, F. Koller, *Prog. Biophys. Mol. Biol.* **1999**, *72*, 19.

[23] W. A. Alves, I. O. Matos, P. M. Takahashi, E. L. Bastos, H. Martinho, J. G. Ferreira, C. C. Silva, R. H. D. A. Santos, A. Paduan-Filho, A. M. D. C. Ferreira, *Eur. J. Inorg. Chem.* **2009**, 2219.

[24] Y. Kono, I. Fridovich, *J. Biol. Chem.* **1983**, *258*, 6015.

[25] G. S. Allgood, J. J. Perry, *J. Bacteriol.* **1986**, *168*, 563.

[26] E. J. Larson, V. L. Pecoraro, *J. Am. Chem. Soc.* **1991**, *113*, 7809.

[27] M. U. Triller, W.-Y. Hsieh, V. L. Pecoraro, A. Rompel, B. Krebs, *Inorg. Chem.* **2002**, *41*, 5544.

[28] J. Gao, A. E. Martell, J. H. Reibenspies, *Inorg. Chim. Acta* **2003**, *346*, 32.

[29] J. Kaizer, T. Csay, G. Speier, M. Réglier, M. Giorgi, *Inorg. Chem. Commun.* **2006**, *9*, 1037.

[30] I. Szilágyi, L. Horváth, I. Labádi, K. Hernadi, I. Pálinkó, T. Kiss, *Cent. Eur. J. Chem.* **2006**, *4*, 118.

[31] F. Karipcin, F. Arabali, I. Karatas, *Russ. J. Coord. Chem.* **2006**, *32*, 109.

[32] A. K. Sra, J.-P. Sutter, P. Guionneau, D. Chasseau, J. V. Yakhmi, O. Kahn, *Inorg. Chim. Acta* **2000**, *300*, 778.

[33] S. Tanasa, M. Andruh, N. Stanica, C. Mathonière, G. Rombaut, S. Golhen, L. Ouahab, *Polyhedron* **2003**, *22*, 1315.

[34] F. Karipcin, B. Dede, S. Percin-Ozkorucuklu, E. Kabalcilar, *Dyes Pigm.* **2010**, *84*, 14.

[35] F. Karipcin, E. Kabalcilar, *Acta Chim. Slov.* **2007**, *54*, 242.

[36] A. Elmottaleb, M. Ramadan, I. M. El-Mehasseb, R. M. Issa, *Transition Met. Chem. (Dordrecht, Neth.)* **1997**, *22*, 529.

[37] N. Sengottuvelan, J. Manonmani, M. Kandaswamy, *Polyhedron* **2002**, *21*, 2767.

[38] N. Mondal, D. K. Dey, S. Mitra, V. Gramlich, *Polyhedron* **2001**, *20*, 607.

[39] F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, 'Advanced Inorganic Chemistry', 6th edn., Wiley-Interscience, New York, NY, USA, 1999.

[40] H. Weihe, H. U. Güdel, *Comments Inorg. Chem.* **2000**, *22*, 75.

[41] F. Karadas, E. J. Schelter, M. Shatruk, A. V. Prosvirin, J. Bacsa, D. Smirnov, A. Ozarowski, J. Krzystek, J. Telser, K. R. Dunbar, *Inorg. Chem.* **2008**, *47*, 2074.

[42] W. E. Entley, G. S. Girolami, *Science (Washington, DC, U.S.)* **1995**, *268*, 397.

[43] C. N. Verani, E. Rentschler, T. Weyhermüller, E. Bill, P. Chaudhuri, *J. Chem. Soc., Dalton Trans.* **2000**, 4263.

[44] P. Chaudhuri, *Coord. Chem. Rev.* **2003**, *243*, 143.

[45] A. Kilic, E. Tas, I. Yilmaz, *J. Chem. Sci.* **2009**, *121*, 43.

[46] A. Bieńko, J. Kłak, J. Mroziński, S. Domagała, B. Korybut-Daszkiewicz, K. Woźniak, *Polyhedron* **2007**, *26*, 5030.

[47] Y. Muranishi, N. Okabe, *Acta Crystallogr., Sect. C* **2002**, *58*, m578.

[48] T. Hirano, R. Okuda, U. Nagashima, P. Jensen, 'Abstracts of OSU International Symposium on Molecular Spectroscopy 2000–2009', http://hdl.handle.net/1811/33326 (date accessed 25th October 2009).

[49] D. X. West, E. J. Zaluzec, S. F. Pavkovic, *Acta Crystallogr., Sect. C* **1994**, *50*, 173.

[50] O. P. Anderson, *Inorg. Chem.* **1975**, *14*, 730.

[51] Y. Naruta, K. Maruyama, *J. Am. Chem. Soc.* **1991**, *113*, 3595.

[52] E. J. Larson, V. L. Pecoraro, *J. Am. Chem. Soc.* **1991**, *113*, 3810.

[53] S. McCann, M. McCann, M. T. Casey, M. Jackman, M. Devereux, V. McKee, *Inorg. Chim. Acta* **1998**, *279*, 24.

[54] M. Devereux, M. McCann, V. Leon, V. McKee, R. J. Ball, *Polyhedron* **2002**, *21*, 1063.

[55] V. Viossat, P. Lemoine, E. Dayan, N.-H. Dung, B. Viossat, *Polyhedron* **2003**, *22*, 1461.

[56] G. Fernández, M. Corbella, M. Alfonso, H. Stoeckli-Evans, I. Castro, *Inorg. Chem.* **2004**, *43*, 6684.

[57] E. J. Larson, V. L. Pecoraro, in: 'Manganese Redox Enzymes', Ed. V. L. Pecoraro, Wiley-VCH, New York, 1992.

[58] M. Sono, M. P. Roach, E. D. Coulter, J. H. Dawson, *Chem. Rev.* **1996**, *96*, 2841.

[59] J. Kaizer, T. Csay, P. Kővári, G. Speier, L. Párkányi, *J. Mol. Catal. A: Chem.* **2008**, *280*, 203.

[60] J. J. P. Stewart, MOPAC 2007, Stewart Computational, Chemistry, Version 7.334W.

[61] J. J. P. Stewart, *J. Mol. Model.* **2007**, *13*, 1173.

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