ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2016, Vol. 61, No. 2, pp. 232–238. © Pleiades Publishing, Ltd., 2016.

PHYSICAL METHODS OF INVESTIGATION

Some Novel Organometallic Mn^{III} Complexes with Porphine and 1,6-Diaminohexane[1]

Shashi Lata Bharati[a], Pankaj Kumar Chaurasia[b], and Sudha Yadava[b]
[a]*Department of Chemistry, North Eastern Regional Institute of Science and Technology, Nirjuli, Arunachal Pradesh, India*
[b]*Department of Chemistry, D.D.U. Gorakhpur University, Gorakhpur-273009, U.P. India*
e-mail: shashilatachem@gmail.com

Received February 16, 2015

Abstract—A novel series of Mn^{III} complexes with 5,10,15,20-tetra(p-tolylporphine) and 1,6-diaminohexane has been synthesized. These complexes have been characterized by UV/Vis, IR, ESI-mass spectra, elemental analysis, conductivity and magnetic susceptibility measurements. These Mn^{III} porphyrins exhibited a blue shift in soret band in comparison to non-metallated porphyrins. The molar conductance values of these complexes show their non-electrolytic nature in ethanol. The tentative structures have also been proposed. All the complexes have good level of water solubility due to which they may have medicinal as well as other valuable biological applications.

Keywords: Mn^{III} porphyrins,1,6-diaminohexane, 5,10,15,20-tetra(p-tolylporphine) ligand, ESI-mass spectra

DOI: 10.1134/S0036023616020212

Metalloporphyrins can experience reversible redox reactions in which the site of electro transfer may be localized at either the central metal or the porphyrin ring [1]. Due to strong complexing properties and catalytic behavior of metalloporphyrins these compounds have found numerous applications in chemical analysis [2]. The use of metalloporphyrins as catalysts in oxidation reactions, like epoxidation of olefins, hydroxylation of saturated hydrocarbon, has been reported previously [3–9]. The Mn^{III} Porphyrins have several interesting aspects of physical, chemical and biological properties which distinguish them from other metalloporphyrins [10–12]. There has been growing interest [13, 14] in Mn^{III} porphyrins because of their reactivity and accessibility of several oxidation states that can be used for redox cycles useful for biochemical applications. They hold a special place in modern chemistry functioning as reaction catalysts, oxygen transporters, chemical sensors [15, 16], anticancer pharmaceutical drugs [17] or in molecular electronic devices [18]. Mn^{III} porphyrins using 5,10,15,20-tetra-phenylporphines have been studied extensively [19–21].

In order to demonstrate different biological applicability of these types of Mn^{III} complexes, it is necessary for them to be dissolved in water to greater extents. If such complexes are found to be dissolved in water then its utility in biological as well as medicinal area will be enhanced. Our previously reported complexes are soluble to water upto 40–60% only. Keeping the above views in mind we have synthesized new Mn^{III} complexes with 5,10,15,20-tetra(p-tolylporphine) ligand and 1,6-diaminohexane as an axial ligand to observe in which way these ligands change the properties of previous reported Mn^{III} porphyrins. In this communication the synthesis and characterization of these novel Mn^{III} porphyrins have been reported.

EXPERIMENTAL

Materials and Physical Measurements

All the chemicals were A.R. Grade and have been purified and dried whenever necessary by the standard methods as given in literature [22–24]. Pyrrole was purchased from Merck (Germany) and acetylacetone from s.d-fine chemicals (Mumbai). Pyrrole and acetyleacetone have been used freshly distilled. Milli-Q water has been used throughout the experimental procedures. The complexes were analysed using standard procedures [25]. The elemental analyses have been done from Cochin University of Science and Technology, Cochin. Conductivity measurements were carried out on century digital conductivity meter; model CC-601 with 10^{-3} M concentration in ethanol at room temperature. Electronic spectra were recorded on Hitachi (Japan) model U-2000 from 200–1100 nm in methanol, using 1 mL quartz cuvette. IR spectra were recorded on Perkin-Elmer (model-557) Beckman-Acculab-10. The magnetic susceptibility measurements were carried out at room temperature using EV7

---

[1] The article is published in the original.

VSM (ADE-DMS-USA) Vibrating Sample Magnetometer from IIT, Kanpur. ESI-mass spectra were recorded on WATERS-Q-T of premier-HAB213 using ethanol as a solvent, from IIT Kanpur. Purity of the complexes were checked by TLC plates, using silica gel adsorbent and CH_2Cl_2/CH_3OH in 1 : 4 ratio.

Synthesis

Preparation of Mn^{III} Porphyrins, $[Mn^{III}(TTP)X]$. The ligand, 5,10,15,20-tetra(p-tolylporphine) has been synthesized by literature method [26]. The synthesis of Mn^{III}-porphyrins have been carried out by adopting a combined literature methods [27, 28]. The bis(acetylacetonato) Mn^{III} complexes with axial halo- or pseudohalo groups i.e. Cl^-, Br^-, NCS^- or N_3^-, serve as useful synthetic intermediates for the synthesis of Mn^{III}-porphyrins [29].

For preparation of $[Mn^{III}(TTP)Cl]$, 1.50 g (0.005 mol) of chlorobis(acetylacetonato) Mn^{III} and 3.5 g. (0.005 mol) of H_2TTP were dissolved in 210 mL of A.R. grade glacial acetic acid containing 60 mL of acetic anhydride and refluxed it for for 4 h. After refluxing, it was evaporated on steam-bath. The resulting bright green complex was dried under vacuum over P_2O_5. Recrystallization was done with 1 : 1 ratio of chloroform and methanol and then air dried. The yield was 3.93 g (78.56%). The Other complexes were prepared analogously. All these complexes are non-hygroscopic in nature.

Preparation of 1,6-diaminohexane complexes, $[Mn^{III}(TTP)X(dah)]$. For preparation of chloro complex, 0.759 g (0.001 mol) of $[Mn^{III}(TTP)Cl]$ was dissolved in 4 mL of ethanol and then added 1.8 g (0.015 mol) of 1,6-diaminohexane. The whole content was stirred for 25 min at room temperature and refluxed for 46 h. The reaction mixture was cooled at room temperature for 1 h and dried under vacuum over P_2O_5. Recrystallizaton was done with ethanol. Yield was 0.667 g (76.32%). The other complexes were prepared under similar conditions.

RESULTS AND DISCUSSION

The Mn^{III} complexes with porphine ligand were synthesized by the following reaction scheme:

$$\begin{array}{c}[Mn^{III}(acac_2)X] + H_2TTP \\ \text{Gla. Acetic acid containing acetic anhydride}\Big\downarrow\text{4 h} \\ [Mn^{III}(TTP)X]\end{array}$$

Where acac = acetylacetonato ligand

$X = Cl^-, Br^-, N_3^-$, or NCS^-

H_2TTP = 5,10,15,20-tetra(p-tolylporphine) ligand.

These $[Mn^{III}(TTP)X]$ complexes were dissolved in ethanol and refluxed with 1,6-diaminohexane to give $[Mn^{III}(TTP)X(dah)]$. The proposed reaction scheme may be given as below:

$$\begin{array}{c}[Mn^{III}(TTP)X] + dah \\ \text{EtOH}\Big\downarrow\text{42–46 h} \\ [Mn^{III}(TTP)X(dah)]\end{array}$$

Where dah = 1,6-diaminohexane.

All these complexes were soluble in ethanol, methanol, pyridine, chloroform, DMSO, DMF and moderately (70%) soluble in water. The molar conductance values of these complexes in ethanol with 10^{-3} M concentration, are in the range of 7–15 Ω^{-1} cm^2 mol^{-1}, indicating their non-electrolytic nature [30]. Physical properties of these complexes have been given in Table 1.

IR Spectra

IR spectra of these complexes shows a medium band at ~1326 cm^{-1} for ν(C=N–) which appears at 1350 cm^{-1} in the free ligand, this downward shift of ~25 cm^{-1} is due to co-ordination of porphine ligand with metal. A sharp band at ~1622 cm^{-1} suggests $\nu(C{=}C)_{pyrrole}$. Other medium bands at ~1179 and ~1571 cm^{-1} indicate ν(C–N) and $\nu(C{=}C)_{phenyl}$ respectively. A broad band at ~3020 cm^{-1} shows $\nu(C{-}H)_{phenyl}$. A sharp band at ~980 cm^{-1} indicates (C–H) rocking mode of pyrrole. All these bands of porphyrin are in good agreement with literature values [31]. The spectra of thiocyanato-tetra(p-tolylporphinato) Mn^{III} shows two characteristics bands of co-ordinated NCS^-, ν(C–S) at ~836 cm^{-1} and ν(C–N) at ~2070 cm^{-1}. The observed value at 836 cm^{-1} falls in the region expected for N-bonded NCS^- (860–780 cm^{-1}) [32], confirming the NCS^- co-ordinated through N. Two characteristics peaks are observed in the azido-tetra(p-tolylporphinato) Mn^{III} complex for co-ordinated azide group assigned as $\nu_{asy}(N{-}N)$ showing strong absorption at 1252 cm^{-1} which usually appears from 1340–1181 cm^{-1} and another peak at ~2025 cm^{-1}, indicating coordination of azide group [33]. All these Mn^{III}-porphyrins exhibit a medium band between 437–492 cm^{-1} for ν(Mn–N) [34, 35].

The $\nu(NH_2)$ of 1,6-diaminohexane are at ~3422 and ~3315 cm^{-1} for free and co-ordinated amine group respectively. Characteristic bands of diamines appear between 1400–700 cm^{-1}. A strong band is observed at ~1325 cm^{-1} assigned to $\omega(NH_2)$. The CN stretch of all uncomplexed diamines are at 1090–1070 cm^{-1} [36]. In these newly synthesized complexes, bands are at 1055–1046 cm^{-1}. This shift indicates co-ordination of

Table 1. Physical properties of synthesized Mn^{III}-porphyrins

Complexes	μ_{eff}	Molar conductance	Yield (%)	Colour	Analysis found (calculated) %							Formula weight
					C	H	N	S	Br	Cl	Mn	
[Mn(TTP)Cl]	4.93	15	78	Bluish green	75.92 (75.34)	4.7 (4.65)	7.38 (6.85)	–	–	4.67 (4.31)	6.2 (6.20)4	759
[Mn(TTP)Br]	4.91	10	79	Bluish green	71.70 (71.35)	4.51 (4.26)	6.97 (6.03)	–	9.94 (9.15)	–	6.83 (6.50)	803
[Mn(TTP)N_3]	4.95	07	78	Bluish green	75.26 (75.02)	4.74 (4.32)	12.8 (12.45)1	–	–	–	7.27 (7.14)	765
[Mn(TTP)NCS]	4.98	11	75	Bluish green	75.25 (73.13)	4.64 (4.31)	8.96 (8.25)	4.10 (4.00)	–	–	7.03 (7.00)	781
[Mn(TTP)Cl(dah)]	4.83	10	76	Blackish purple	70.04 (70.00)	5.99 (5.30)	9.60 (9.32)	–	–	4.05 (4.01)	6.27 (6.13)	875
[Mn(TTP)Br(dah)]	4.80	11	66	Black	70.49 (70.31)	5.70 (5.63)	9.14 (9.12)	–	8.69 (8.39)	–	5.9 (5.35)	919
[Mn(TTP)N_3(dah)]	4.75	13	57	Brownish purple	73.52 (73.59)	5.94 (5.64)	14.30 (14.25)	–	–	–	6.23 (6.12)	881
[Mn(TTP)NCS(dah)]	4.70	10	67	Brownish purple	73.54 (73.31)	8.30 (8.56)	10.92 (10.67)	3.57 (3.60)	–	–	6.12 (6.02)	897

Table 2. Selected IR spectral results (cm^{-1}) of Mn$^{\text{III}}$-porphyrins

Mn(TTP)Cl	Mn(TTP)Br	Mn(TTP)N$_3$	Mn(TTP)NCS	Assignment
490	492	488	491	ν(Mn–N)
1606	1604	1608	1604	ν(C=C) $_{\text{py}}$
1304	1306	1304	1308	ν(C=N)$_{\text{py}}$
1183	1181	1184	1184	ν(C–N)$_{\text{py}}$
1520	1518	1515	1518	ν(C=C) $_{\text{ph}}$
3021	3022	3023	3022	ν(C–H)$_{\text{ph}}$
1440	1442	1440	1443	ν_{antisym}(C–H) of CH$_3$
–	–	–	2070	ν(NCS)
–	–	2025	–	ν(N$_3$)

Table 3. Selected IR spectral results (cm^{-1}) of Mn$^{\text{III}}$-porphyrins

[Mn(TTP)Cl(dah)]	[Mn(TTP)Br(dah)]	[Mn(TTP)N$_3$(dah)]	[Mn(TTP)NCS(dah)]	Assignment
475	473	473	475	ν(Mn–N)
1613	1611	1610	1610	ν(C=C)$_{\text{py}}$
1323	1328	1325	1328	ν(C=N)
1168	1168	1170	1170	ν(C–N)
1512	1510	1512	1510	ν(C=C)$_{\text{ph}}$
3028	3029	3028	3030	ν(C–H)$_{\text{ph}}$
1425	1423	1423	1425	ν_{antisy}(C–H) of CH$_3$
–	–	–	2073	ν(NCS)
–	–	2023	–	ν(N$_3$)
3325	3323	3323	3325	ν(NH$_2$)$_{\text{co-ordinated}}$
3422	3421	3421	3422	ν(NH$_2$)$_{\text{unco-ordinated}}$
[Mn(TTP)Cl(dah)]	[Mn(TTP)Br(dah)]	[Mn(TTP)N$_3$(dah)]	[Mn(TTP)NCS(dah)]	Assignment

diamines nitrogen to manganese. The NH$_2$ rocking mode is a strong band at ~635 cm^{-1}. The ν(C–C) has been assigned as a strong band at ~1000 cm^{-1} [37]. The above data indicates that 1,6-diaminohexane co-ordinates as an unidentate ligand to Mn$^{\text{III}}$ (Tables 2, 3).

Electronic Spectra

Electronic spectra of the porphyrins exhibit an intense band near 400 nm that are assigned as soret or B band. Several weaker absorptions also occur near 480–700 nm which are known as Q bands.

For [Mn$^{\text{III}}$(TTP)X] complexes, the B band appear with λ_{max}(nm) at 455, 453, 450 and 452 and Q bands with λ_{max}(nm) at 648, 644, 642 and 645, while for [Mn$^{\text{III}}$(TTP)X(dah)] complexes, the B band appear with λ_{max}(nm) at 449, 445, 460 and 455 and Q bands with λ_{max}(nm) at 666, 665, 678, 666 for X = Cl$^-$, Br$^-$, N$_3^-$ and NCS$^-$ respectively [38, 39] (Table 4). The intense band at 445–460 nm in electronic spectra of these complexes are assigned to charge transfer band from a$_{1u}$(π) and a$_{2u}$(π) orbital of porphyrin to e$_g$(dπ) orbital of manganese [40–42].

The ligand field parameters i.e. 10Dq, B and β have also been calculated for these Mn$^{\text{III}}$-porphyrins. The value of 10Dq have been calculated from λ_{max} at maximum absorbance. The value of B has been calculated by using the formula Dq/B = 2.7 using the Tanabe–Sugano diagram while β has been calculated using the formula

$$\beta = B_{\text{in complex}}/B_{\text{free ion}}.$$

Table 4. UV-visible spectroscopic data of free base porphyrin and Mn^{III}-porphyrins

Ligand/complexes	λ_{max} (nm)	
	Soret (B) band	Q band
H_2TTP	484	651
[Mn(TTP)Cl]	455	648
[Mn(TTP)Br]	453	644
[Mn(TTP)N_3]	450	642
[Mn(TTP)NCS]	452	645
[Mn(TTP)Cl(dah)]	449	666
[Mn(TTP)Br(dah)]	445	665
[Mn(TTP)N_3(dah)]	460	678
[Mn(TTP)NCS(dah)]	455	666

The value of B are below the free ion value for Mn^{III}-ion (1140 cm^{-1}) [43], this indicates the covalent metal-ligand bonds in all these complexes, with the covalency factor β varying in the range 0.71–0.81 (Table 5).

ESI-Mass Spectra

ESI-mass spectra was used for identity and purity of these Mn^{III}-porphyrins [44–46]. The different molecular ion peaks found for different complexes and data is given below: *m/z* at 723 for $[C_{48}H_{36}N_4Mn–Cl]^+$ molecular ion, *m/z* 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion, for the complex [Mn(TTP)Cl], *m/z* at 724 for $[C_{48}H_{36}N_4Mn + H]^+$ molecular ion, *m/z* at 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion for the complex [Mn(TTP)Br], *m/z* at 723 for $[C_{48}H_{36}N_4Mn]^+$ molecular ion, *m/z* at 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion for the complex [Mn(TTP)N_3], and *m/z* at 724 for $[C_{48}H_{36}N_4Mn + H]^+$ molecular ion, *m/z* at 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion for the complex [Mn(TTP)NCS].

While *m/z* at 839 for $[C_{54}H_{52}N_6Mn–Cl]^+$ molecular ion, *m/z* at 725 for $[C_{48}H_{36}N_4Mn + 2H]^+$ molecular ion and *m/z* at 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion for the complex [Mn(TTP)Cl(dah)], *m/z* at 803 for $[C_{48}H_{36}N_4BrMn]^+$ molecular ion, *m/z* at 725 for $[C_{48}H_{36}N_4Mn + 2H]^+$ molecular ion and *m/z* at 670 for $[C_{48}H_{36}N_4 +2H]^+$ molecular ion for the complex [Mn(TTP)Br(dah)], *m/z* at 766 for $[C_{48}H_{36}N_7Mn + H]^+$ molecular ion, *m/z* at 723 for $[C_{48}H_{36}N_4Mn]^+$ molecular ion and *m/z* at 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion for the complex [Mn(TTP)N_3(dah)] and *m/z* at 781 for $[C_{49}H_{36}N_5SMn]^+$ molecular ion, *m/z* at 724 for $[C_{48}H_{36}N_4Mn + H]^+$ molecular ion and *m/z* at 670 for $[C_{48}H_{36}N_4 + 2H]^+$ molecular ion was found for the complex [Mn(TTP)NCS(dah)].

Table 5. Different ligand field parameters calculated for different Mn^{III}-porphyrins

Complexes	10Dq (cm^{-1})	B (cm^{-1})	β
[Mn(TTP)Cl]	21978	814	0.71
[Mn(TTP)Br]	22075	815	0.71
[Mn(TTP)N_3]	22022	822	0.72
[Mn(TTP)NCS]	22123	819	0.71
[Mn(TTP)Cl(dah)]	23923	885	0.77
[Mn(TTP)Br(dah)]	25000	925	0.81
[Mn(TTP)N_3(dah)]	22042	816	0.71
[Mn(TTP)NCS(dah)]	23570	872	0.76

Magnetic Susceptibility

The magnetic susceptibility measurements show that these complexes have μ_{eff} values in the range of 4.70–4.98 μB [47]. The presence of four unpaired electrons indicates the high spin Mn^{III} complexes with porphyrins.

CONCLUSION

The manganese^{III} complexes with 5,10,15,20-tetra(p-tolylporphine) ligand have been prepared for the first time. On the basis of positions of ν(NH_2) in IR spectra of [Mn^{III}(TTP)X(dah)] complexes, it was concluded that 1,6-diaminohexane is co-ordinated to Mn^{III} as unidentate ligand. The ESI-mass spectra indicates that these complexes are monomeric in nature having octahedral geometry, while the [Mn^{III}(TTPX] complexes have square pyramidal geometry as reported earlier [38, 39]. The previously synthesized Mn^{III}-porphyrins have shown depolymerisation activity towards Humic acid model compound, in the same way these newly synthesized Mn^{III} porphyrins can be studied for their depolymerisation activity which can also be used as a feedstock for preparation of commodity and rare chemicals. One important finding of this manuscript is that all the synthesized Mn^{III} complexes of this manuscript are soluble in water to much more extent in comparison to our previously synthesized complexes (~70%) which may be valuable from the points of view of their biological studies. Studies of biological and medicinal importance on the basis of their solubility in water are in progress.

ACKNOWLEDGMENTS

Dr. Shashi Lata Bharati is grateful to Department of Chemistry, DDU Gorakhpur University, Gorakh-

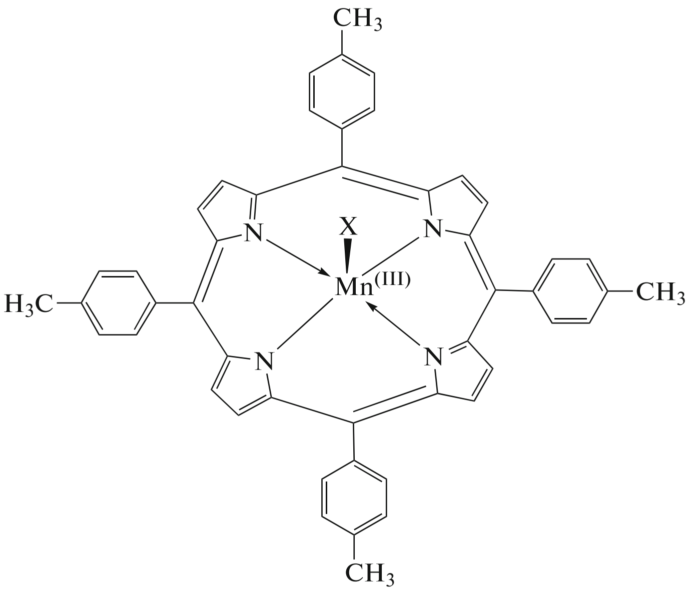

Fig. 1. [Mn^{III}(TTP)X] complexes.

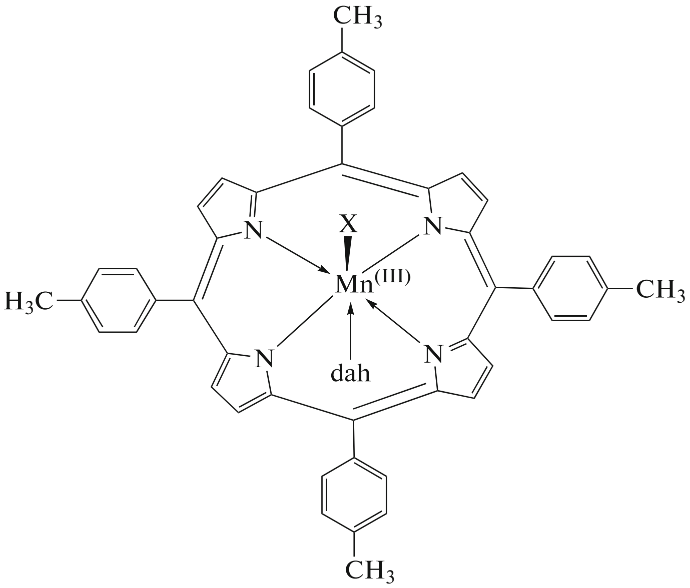

Fig. 2. [Mn^{III}(TTP)X(dah)] complexes.

pur for the award of UGC-DSA fellowship during her Ph.D. The academic support of Prof. V.K. Yadav and Prof. S.S. Manoharan, Department of Chemistry, IIT Kanpur, for recording ESI-mass spectra and magnetic susceptibility measurements, respectively, is gratefully acknowledged.

REFERENCES

1. S. Jeon H. K. Lee, and Yong-Cook Chai, Bull. Korean Chem. Soc. **17**, 929 (1996).
2. M. Biesaga, K. Pyrzynska, and M. Trojanowicz, Talanta **51**, 209 (2000).
3. Meunier B., Chem Rev. **92**, 1411 (1992).
4. Quici S., Banafi S., Pozzi G., Gazz. Chim. Ital., **123**, 597 (1993).
5. Mansuy D., Pure Appl. Chem. **66**, 737 (1994).
6. *Metalloporphyrins in Catalytic Oxidations*, Ed. by R. A. Sheldon (Marcel Dekker, New York, 1994).
7. *Metalloporphyrins Catalysed Oxidations*, Ed. by F. Montanari and L. Casella (Kluwer, Dordrecht, 1994).

8. A. M. R. Gonsalves and M. M. Pereira, J. Mol. Catal. A: Chem. **113**, 209 (1996).
9. D. Dolphin, T. G. Traylor, and L. Y. Xie, Acc. Chem. Res. **30**, 251 (1997).
10. B. M. Hoffman, C. J. Weschler, and F. Basolo, J. Am. Chem. Soc. **100**, 4416 (1978).
11. A. Harriman, J. Chem. Soc, Dalton Trans., 141 (1984).
12. T. Jin, T. Suzuki, T. Imamura, and M. Fujimoto, Inorg. Chem. **26**, 1280 (1987).
13. L. F. Lauffer, Chem. Rev. **87**, 901 (1987).
14. M. Ravikanth and T. K. Chandrashekhar, Struc. Bond. **82**, 105 (1995).
15. E. Malinowaska, J. Niedziolka, and M. E. Meyerhoff, Anal. Chim. Acta **432**, 67 (2001).
16. D. Vlascici, E. Fagadar-Cosma, and O. Bizerea-Spirido, Sensors **6**, 892 (2006).
17. H. Brunner and K. M. Schellerer, Monatch. Chem. **133**, 679 (2002).
18. C. M. Drain, J. T. Hupp, K. S. Suslick, et al., J. Porph. Phthal. **6**, 243 (2002).
19. Day V.W., Stults B.R., Tassett E.L., et al., J. Inorg. Nucl. Chem. Lett. **11**, 505 (1975).
20. A. Tulinsky and B. M. L. J. Chen, J. Am. Chem. Soc. **197799**, p. 3647.
21. J. F. Kirner and W. R. Scheidt, Inorg. Chem. **14**, 2081 (1975).
22. R. J. Errington, *Advanced Practical Inorganic and Metalloorganic Chemistry*, 1st Ed. (Chapman and Hall, London, 1997).
23. W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals*, 4th Ed. (Butterworth-Heinemann, Oxford, 1997).
24. B. S. Furniss, A. J. Hannaford, V. Rogers, et al., *Vogel's Text Book of Practical Organic Chemistry*, 4th Ed. (ELBS, London, 1984).
25. G. H. Jeffery, J. Bassett, J. Mendham, and R. C. Denny, *Vogel's Text Book of Quantitative Chemical Analysis*, 5th Ed. (ELBS, London, 1996).
26. A. D. Adler, F. R. Longo, J. D. Finarelli, et al., J. Org. Chem. **32**, 476 (1967).
27. E. B. Fleischer, J. M. Palmer, T. S. Srivastava, and A. Chatterjee, J. Am. Chem. Soc., **93**, 3163 (1971).
28. B. R. Stults, V. W. Day, E. L. Tassett, and R. S. Marianelli, Inorg. Nucl. Chem. Lett. **9**, 1259 (1973).
29. B. R. Stults, V. W. Day, and R. S. Marianelli, Inorg. Chem. **14**, 722 (1975).
30. S. F. A. Kettle, *Coordination Compounds* (Nelson, Pitman Press, London, 1975).
31. D. W. Thomas and A. E. Martell, J. Am. Chem. Soc. **78**, 1338 (1956).
32. R. J. H. Clark and C. S. Williams, Spectrochim. Acta **22**, 1081 (1966).
33. J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds* (Prentice-Hall of India Private, New Delhi, 1969).
34. T. N. Lomova and B. D. Berezin, Russ. J. Coord. Chem. **27**, 85 (2001).
35. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, *Comprehensive Coordination Chemistry* (Pergamon, Oxford, 1987), Vol. 1, p. 816.
36. I. Gamo, Bull. Chem. Soc. Jpn. **34**, 760 (1961).
37. A. D. Allen and C. V. Senoff, Can. J. Chem. **45**, 888 (1965).
38. S. Yadava and S. L. Bharati, J. Coord. Chem. **64**, 3950 (2011).
39. S. Yadava and S. L. Bharati, J. Coord. Chem. **65**, 3492 (2012).
40. E. Fagadar-Cosma, M. C. Mirica, I. Balcu, et al., Molecules, **14**, 1370 (2009).
41. Y. Lamamoto, M. D. Assis, K. J. Ciuffi, et al., J. Mol. Catal. A: Chem. **116**, 365 (1997).
42. H. A. O. Hill, A. J. MacFarlane, and R. J. P. Williams, J. Chem. Soc., 1704 (1969).
43. J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry, Principles of Structure and Reactivity*, 4th Ed. (Pearson Education, Singapore, 2005).
44. I. Batinic-Haberle, I. Spasojevic, R. D. Stevens, et al., Dalton Trans., 617 (2006).
45. I. Batinic-Haberle, I. Spasojevic, R. D. Stevens, et al., J. Chem. Soc., Dalton Trans. 2689 (2002).
46. I. Batinic-Haberle, I. Spasojevic, R. D. Stevens, et al., Dalton Trans. 1696 (2004).
47. D. V. Behere and S. Mitra, Inorg. Chem. **19**, 992 (1980).