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Structural Elucidation Studies on Transition Metal Complexes of New Hydrazino Quinoxaline Derivatives

P.V. ANANTHALAKSHMI, D. SANDHYARANI and V. JAYATYAGARAJU*
Department of Chemistry
Osmania University, Hyderabad 500 007, India

Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes of new tridentate oxygen-nitrogen donors, N-salicylidene-3-hydrazino quinoxalin-2-one (HSHQO) and N-(2-hydroxy)-acetophenonyl 3-hydrazinoquinoxalin-2-one (HHAHQO), have been prepared and characterized by elemental analysis, conductance, thermal, spectral and magnetic data. HSHQO acts as a monobasic tridentate ONN donor through the phenolic oxygen and azomethine nitrogens where as HHAHQO acts as a monobasic ONO donor through the phenolic oxygen, azomethine (free) nitrogen and carbonyl oxygen in all the complexes.

INTRODUCTION

Literature survey reveals that metal complexes of fused nitrogen heterocyclic compounds like quinoxaline[1, 2], its dione[3, 4] and corresponding derivatives[5–7], particularly those having azomethine centres of coordination have received less attention inspite of their potential metal binding properties and promising applicabilities. The preparation of tridentate oxygen, nitrogen donor systems containing 1,4-quinoxaline and their metal complexes has been undertaken in order to evaluate the insecticidal and antimicrobial properties of these compounds. The present paper discusses the synthesis and characterisation of N-salicylidene-3-hydrazino quinoxaline 2-one (HSHQO), N-(2-hydroxy) acetophenonyl-3-hydrazino quinoxaline-2-one (HHAHQO), and their complexes with chromium(III), manganese(III), iron(III), cobalt(II), nickel(II) and copper(II).

EXPERIMENTAL

AnalaR grade metal chlorides were used as supplied. Salicylaldehyde and 2-hydroxy acetophenone were obtained from fluka, solvents were purified by established procedures.

Mass spectra were recorded on a Perkin-Elmer Hitachi RMU-6L spectrometer and ^{1}H nmr spectra were recorded on Varian XL-200 MHz in DMSO-d_6. IR spectra (KBr discs) were recorded in the 4000–400 cm^{-1} region on Shimadzu IR-435 and in Nujol media in the 4000–200 cm^{-1} region on Perkin-Elmer 283-B and reflectance spectra of solids were recorded on a Cary-2390 instrument. Magnetic susceptibilities were measured on a Faraday balance CAHN-7550–03 USA at room temperature using $Hg[Co(NCS)_4]$ as calibrant. Diamagnetic correction using Pascal's constants and temperature independent paramagnetic corrections were computed[8]. The electrical conductance measurements were recorded using 10^{-3} molar solutions in DMSO with an Elico conductivity bridge (Model CM-180) and dip type cell calibrated with KCl solutions. The presence of coordinated water was established for some complexes by DTA and TGA. DTA was carried out on the lead and Northrup-USA instrument and TGA on Perkin-Elmer model TGS-2 instrument. EPR were recorded on Jeol SE-3X (X-band) spectrometer at RT and LNT.

Synthesis of HSHQO: HSHQO was prepared by a three-step process involving the synthesis of quinoxaline-2, 3-dione[9] (QD) and 3-hydrazino quinoxaline-2-one (HQO)[10].

3-Hydrazino-quinoxaline-2-one (8.8 g) was dissolved in hot methanol to which salicylaldehyde 6 mL) was added and the mixture was refluxed for 1 h. The bright yellow product that separated out in hot condition was filtered and washed successively with methanol and petroleum ether. The product was recrystallised from aqueous methanol and dried *in vacuo.* (Fig. 1)

Yield: 11 g, m.p. 296°C (Found: C, 64.4; H, 4.15; N, 20.4; $C_{15}H_{12}N_2O_2$ Calcd: C, 64.4; H, 4.3; N, 20.0%) *m/z* 280.

^{1}H NMR (DMSO–d_6): 11.8[10] (OH and ring NH) (2), 6.8–7.6 (aromatic and NH of hydrazone fragment)[9], 8.7 (azomethine CH) (1). IR bands (cm^{-1}): 3150 (νNH of hydrazone fragment), 3050 cm^{-1} (νOH), 2900 cm^{-1} (νNH of quinoxaline ring)[11], 1690 cm^{-1} (νC = O)[12] multistructured band at 1620 cm^{-1}, 1600 cm^{-1} and 1580 cm^{-1} (νNH, νC = N (free) and νC = N ring), 1346 cm^{-1}, νC—O, 1000 cm^{-1} (νN—N). UV-Vis (λ_{max} in cm^{-1}): 45454 (benzene moiety, 28985 (lactam carbonyl), 25974 and 24691 (ring and free azomethine).

Synthesis of HHAHQO: The HHAHQO ligand was prepared by a three step process from the synthesis of quinoxaline-2, 3-dione[9] (QD) and 3-hydrazino quinoxaline-3-one (HQO)[10].

HQO (8.8 g) was dissolved in hot methanol and 2-hydroxy acetophenone (28 ml) was added. The reaction mixture was refluxed for 15 h. Then the solution was concentrated to half the volume under reduced pressure to obtain soft, lemon yellow crystalline product. It was filtered and washed with methanol and petroleum ether. The compound was recrystallised from methanol dried *in vacuo.* (Fig. 1).

Yield: 7.6 g, m.p. 260°C (Found: C, 65.3; H, 4.9; N, 19.2; $C_{16}H_{14}N_2O_2$ Calcd: C, 65.3; H, 4.8; N, 19.0% *m/z* 294.

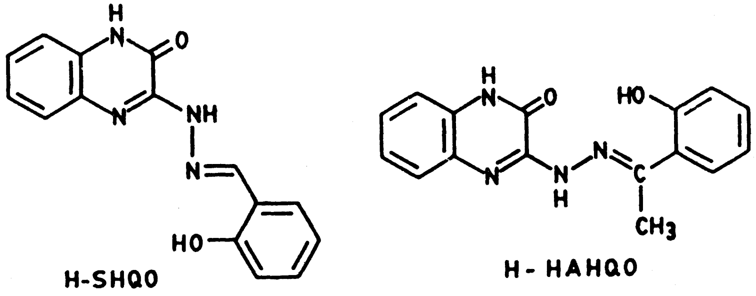


Fig. 1. Structures of ligands-HSHQO, H-HAHQO

^{1}H NMR (DMSO–d_6): 13.1 (OH) (1), 12.3 (ring NH) (1), 6.8–8.8 (aromatic and NH (hydrazone)] (9), 2.5 (methyl) (3). IR bands (cm^{-1}): 3000–2850 cm^{-1} (combination band of (νC = N free) and νC = N (ring), 1210 cm^{-1} (C—O), 1020 cm^{-1} (νN—N). UV-Vis (λ_{max} in cm^{-1}): 43478 (benzene moiety, 32258 (lactam carbonyl), 25316 and 24096 (free and ring azomethines).

Preparation of the complexes: A general method was adopted for the preparation of all the complexes. To the methanolic solution of the metal chloride, methanolic suspension of the ligand was added in small increments. After complete addition the metal to ligand mole ratio was always kept as 1:2. It was observed that the ligand dissolves completely in the presence of metal ion and a clear solution was obtained after each addition. The pH of the reaction mixture was then raised to 7 using 1% alcoholic ammonia solution. The reaction mixture was refluxed for 3–4 h. The coloured product obtained was filtered in hot condition and washed successively with small increments of methanol, petroleum ether and ether and dried *in vacuo*. The purities of ligands and metal complexes were checked by tlc. The analytical data and proposed formulae for the complexes are given in Table 1.

RESULTS AND DISCUSSION

The HSHQO, HHAHQO complexes are coloured and stable in atmosphere. They are insoluble in common organic solvents but soluble in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). They decomposed at high temperatures. Analytical data indicate that the metal to ligand stoichiometry is 1:1 in chromium(III), manganese(II), iron(III) complexes of HSHQO and chromium(III), copper(II) complexes of HHAHQO; a ratio of 1:2 in cobalt(II), nickel(II), copper(II) complexes of HSHQO and iron(III), cobalt(II), nickel(II), copper(II) complexes of HHAHQO. The M:L is 2:3 in manganese(II) complex of HHAHQO. Chromium(III) and iron(III) complexes are 1:1 electrolytes[13] (Table-1). From the elemental analysis and conductivities, it can be concluded that, in chromium(III) and iron(III) complexes, out of two chlorides only one is ionisable while the other is in the coordination sphere. It is also concluded that in manganese(II) complexes and copper(II) complex of HHAHQO, chloride ion is within the coordination sphere. The presence of coordinated water in chromium(III) complexes of HSHQO and HHAHQO, manganese(II), iron(III) complexes of HSHQO was established by TGA and DTA.

IR spectra

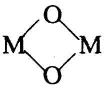
HSHQO complexes: The IR spectral data of the complexes are presented in Table-1. All the complexes show changes in ν(C—O), ν(N—N), ν(C=N) (ring) and ν(C=N) (exo) indicating binding to the metal through an ONN[14–17] sequence involving phenolic oxygen and azomethine nitrogens. As the complexes are isolated in neutral media the deprotonation of phenolic group is unavoidable. No band is observed at 3050 cm^{-1} in cobalt(II), nickel(II) and copper(II) complexes, suggesting the cleavage of intramolecularly hydrogen bonded —OH with subsequent deprotonation and coordination through phenolic oxygen[18, 19]. The mul-

TABLE-1
ANALYTICAL AND IR SPECTRAL DATA OF METAL COMPLEXES OF H-HAHQO

Complex (formula)	M_2 mho cm^2 mole^{-1}	Found (Calcd) %			vNH	vNH (ring)	v(OH+NH)	v(C=O)	v(C=N) (free)	v(C═N) (ring)	v(C–O) (phenolic)	v(N—N)	New bands
		M	N	Cl									
Cr(III)SHQO ($CrC_{15}H_{15}N_4O_4Cl_2$)	42	11.65 (11.87)	12.68 (12.78)	16.19 (16.21)	—	—	2850–3500	1690	1570	1500	1370	1030	907, 597, 548, 327, 307, 302
Mn(II)SHQO ($MnC_{15}H_{13}N_4O_3Cl$)	17.2	13.98 (14.19)	14.32 (14.45)	9.05 (9.16)	—	—	2700–3600	1690	1570	1520	1360	1040	950, 540, 480, 320, 310
Fe(III)SHQO ($FeC_{15}H_{15}N_4O_4Cl_2$)	76.2	12.19 (12.47)	12.54 (12.69)	15.88 (16.09)	—	—	2900–3400	1690	1570	1530	1360	1030	900, 490, 440, 330, 305
Co(II)SHQO ($CoC_{30}H_{22}N_8Cl_4$)	8.4	9.42 (9.59)	17.92 (18.21)	—	3200	2950	—	1690	1570	1520	1360	1030	636, 602
Ni(II)SHQO ($NiC_{30}H_{22}N_8O_4$)	14.2	8.75 (9.59)	18.18 (18.21)	—	3200	3000	—	1690	1560	1525	1360	1030	562, 520, 508, 471
Cu(II)SHQO ($CuC_{30}H_{22}N_8O_4$)	23.1	9.55 (10.28)	17.78 (18.00)	—	3200	3000	—	1690	1570	1520	1360	1060	570, 510, 420

Complex (formula)	M_2 mho cm^2 $mole^{-1}$	Found (Calcd) %			νNH	νNH (ring)	ν(OH+NH)	ν(C=O)	ν(C=N) (free)	ν(C=N) (ring)	ν(C–O) (phenolic)	ν(N—N)	New bands
		M	N	Cl									
Cr(III)HAHQO ($CrC_{16}H_{17}N_4O_4Cl_2$)	57	11.31 (11.50)	12.27 (12.38)	15.68 (15.71)	—	—	2800–4300	1660	1600	1558	1220	1040	840, 580, 540, 500, 330
Mn(II)HAHQO ($MnC_{48}H_{39}N_{12}O_6Cl$)	14	10.51 (10.73)	16.16 (16.39)	3.45 (3.47)	3350	3200	—	1650	1605	1558	1240	1040	610, 474, 2345, 232, 228
Fe(III)HAHQO ($FeC_{32}H_{26}N_8O_4Cl$)	59	8.25 (8.26)	16.22 (16.53)	5.11 (5.23)	3400	3050	—	1650	1600	1558	1240	1060	666, 614
Co(II)HAHQO ($CoC_{32}H_{26}N_8O_4$)	26	8.97 (9.15)	17.28 (17.36)	—	3400	3300	—	1660	1590	1560	1240	1050	610, 570, 540, 490
Ni(II)HAHQO ($NiC_{32}H_{26}N_8O_4$)	8	9.14 (9.15)	17.24 (17.36)	—	3400	3300	—	1650	1590	1560	1240	1060	620, 600, 540, 520, 495
Cu(II)HAHQO ($CuC_{16}H_{13}N_4O_2Cl$)	9	16.09 (16.31)	14.25 (14.27)	9.04 (9.05)	3300	3200	—	1650	1590	1560	1240	1040	636, 609, 555, 549, 330

All IR bands in cm^{-1}; abbreviation H-SHQO = N-salicylidene 3-hydrazino-1, 4-quinoxaline-2-one H-HAHOQ = N-(2-hydroxy acetophenonyl)-3-hydrazino-1, 4-quinoxaline-2-one tistructured broad band in the region of 3600–2600 cm^{-1} in chromium(III), manganese(II) and iron(III) complexes is attributed to νNH, ν(C—H) and νOH (of coordinated water)[20] and the appearance of non-ligand band in the region 960–950 cm^{-1} confirms[21] the presence of coordinated water. The new bands in the far IR region are attributed to ν(M—O), and ν(M—N) in all the complexes and 330–300 cm^{-1} to ν(M—Cl)[22] in chromium(III), manganese(II) and iron(III) complexes.

HHAHQO Complexes: During complexation the hydrogen bonds get served and as such νNH is shifted to higher frequency in all the complexes except chromium(III). As the complexes were isolated in neutral meedia, the deprotonation of phenolic group is a reasonable conclusion and as such νOH does not appear in the spectra. It is difficult to identify the changes regarding these bands in IR spectra of chromium(III) complex as there is broad band in the region of 3400–2800 cm^{-1} which can be assigned to a νOH (of coordinated water)[20] as confirmed by thermal analysis and the appearance of non-ligand band at 840 cm^{-1} due to the rocking mode. This band may also include the components of NH (ring, free). Phenoxide binding in all the complexes is further confirmed by the upward shift of ν(C—O)[14]. Negative shifts observed in ν(C═O)[23] and ν(C═N) (exo) and upward shift ν(N—N)[15] indicate binding through carboxyl oxygen and one of the azomethie nitrogens. It can be concluded that the ligand H-HAHQO acts as a monobasic tridentate ONO donor in all the complexes. The new bands in the far IR region are attributed to ν(M—O) and ν(M—N) modes. The ν(M—Cl) is identified at *ca.* 330 cm^{-1} in chromium(III) and copper(II) complexes. There is a new peak at 749 cm^{-1} in manganese(II) complexes which is attributed to  mode[24, 25]

It is interesting to mode that the ligands H-SHQO, H-HAHQO which differ with respect to one hydrogen and a methyl group could offer variable metal binding sets *i.e.*, ONN and ONO respectively. This probably points towards the preferred conformations of the ligands in the binding processes. H-SHQO's preference for ONN donation may suggest stabilization of the chelates due to intramolecular hydrogen bonding involving lactam oxygen or hydrazino nitrogen and azomethine nitrogen. The same is probably not true with the bulky, electron releasing methyl group.

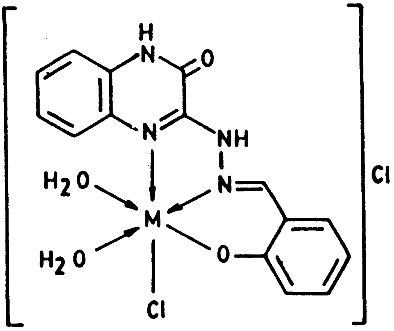
Magnetic moments and electronic spectral data

Magnetic moments and electronic spectral data are given in Table-2. Except for manganese(II) complex of H-HAHQO the magnetic moments are in good agreement with the presence of unpaired electrons expected for spin free complexes. Manganese(II) complex of H-HAHQO exhibits effective magnetic moment of 4.97 B.M. which is lower than the expected spin only value for five unpaired electrons. The sub-normal moment is attributed to the possible M—M interactions[26] in the dimeric structure, resulting due to oxygen bridging. Electronic spectal data are consistant with the proposed geometries.

TABLE-2
MAGNETIC MOMENT AND ELECTRONIC SPECTRAL DATA OF METAL COMPLEXES OF H-SHQO AND H-HAHQO

Complex	μ_{eff} (B.M.)	ν_{max} (cm^{-1})	Assignments
Cr(III)SHQO	4.15	31250 25641 14492	$^4A_{2g} \rightarrow {}^4T_{1g}(P)$ $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ $^4A_{2g} \rightarrow {}^4T_{2g}$
Mn(II)SHQO	6.06	28600–12000	
Fe(III)SHQO	5.81	32258, 30303 26500, 20408–12500	
Co(II)SHQO	4.71	22727, 21276 17543 8695	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ $^4T_{1g} \rightarrow {}^4A_{2g}$ $^4T_{1g} \rightarrow {}^4T_{2g}$
Ni(II)SHQO	3.13	20833 17543 12820 8695	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ $^3A_{2g} \rightarrow {}^1E_g$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{2g}$
Cu(II)SHQO	1.87	20000 17543 15625	$^4B_{2g} \rightarrow {}^2A_{1g}$ $^4B_{2g} \rightarrow {}^2B_{1g}$ $^4B_{2g} \rightarrow {}^2E_g$
Cr(II)HAHQO	3.80	333333–31250 26315 16129	$^2A_{2g} \rightarrow {}^4T_{1g}(P)$ $^2A_{2g} \rightarrow {}^4T_{1g}(F)$ $^2A_{2g} \rightarrow {}^4T_{2g}$
Mn(II)HAHQO	4.97	33333, 294411, 27777 25974, 20833, 17543 15625, 15151	—
Fe(III)HAHQO	5.83	31250, 28571 25641, 20833	—
Co(II)HAHQO	3.98	21000–17000 15625 8196	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$ $^4T_{1g} \rightarrow {}^4T_{2g}$ $^4T_{1g} \rightarrow {}^4T_{2g}$
Ni(II)HAHQO	2.81	26315 15625 11111	$^3A_{2g} \rightarrow {}^3T_{1g}(P)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{2g}$
Cu(II)HAHQO	1.79	20833 16666 14925	$^2B_{1g} \rightarrow {}^2E_g$ $^2B_{1g} \rightarrow {}^2A_{1g}$ $^2B_{1g} \rightarrow {}^2B_{2g}$

Five coordinate geometry of Mn(II)·SHQO complex: Reports on high-spin manganese(II) five coordinate complexes are very scanty. Though, detailed studies are not available, ciampolini[27] and others have reported complexes with



M = Cr^{III}, Fe^{III}

Fig. 2. HSHQO Cr(III) and Fe(III) complexes

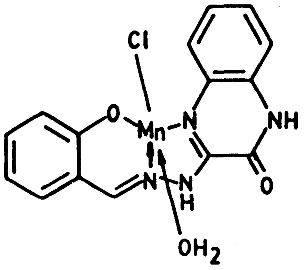
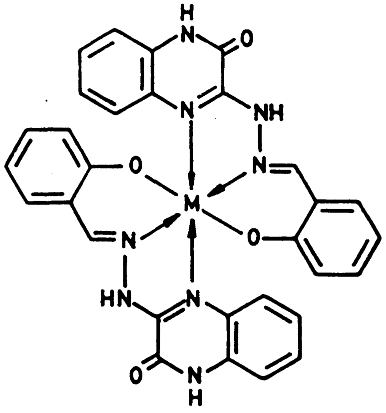
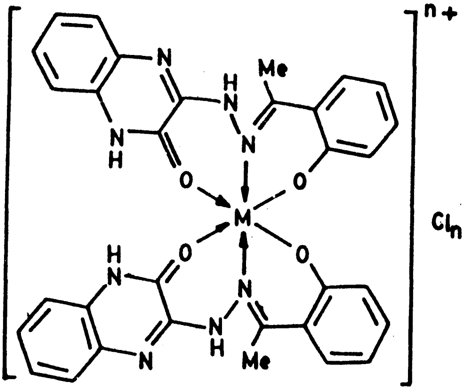


Fig. 3. HSHQO Mn(II) complex



M = Co^{II}, Ni^{II}, Cu^{II}

Fig. 4. HSHQO Co(II), Ni(II) and Cu(II) complexes



M = Fe^{III}, n = 1

M = Co^{II}, Ni^{II}, n = 0

Fig. 5. HHAHQO Fe(III), Co(II) and Ni(II) complexes

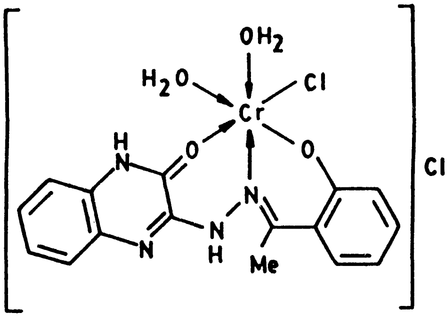


Fig. 6. HHAHQO Cr(II) complex

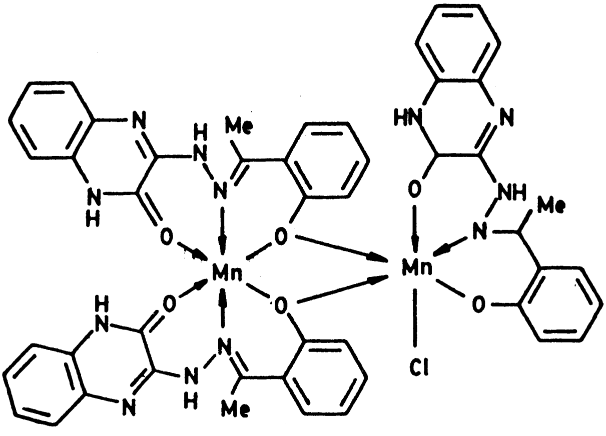


Fig. 7. HHAHQO Mn(II) complex

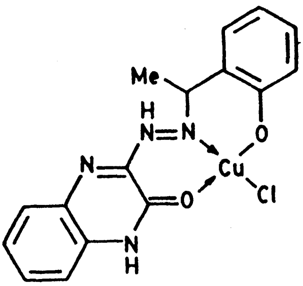


Fig. 8. HHAHQO Cu(II) complex

terdentate ligands like bis(2-di-methylaminoethyl)methylamine. The electronic spectrum of the Mn(II)-SHQO complex does not fit in octahedral or tetrahedral geometry. The analytical data also do not support these geometries. The Mn(II)·SHQO complex with composition [MnL·H_2O·Cl] can be adjudged to have five coordinate stereochemistry. The magnetic moment 6.06 B.M. fits well into high spin five coordinate, trigonal bipyramidal geometry[28]. Comparable to an earlier reported five coordinated manganese(II) complex, the present complex exhibits several weak absorptions in the range fo 12000–28600 cm^{-1}. Based on these observations, manganese(II) complexes has been assigned five coordinated trigonal bipyramidal geometry.

EPR spectra of Cu(II) complexes: The EPR spectrum of Cu(II) SHQO complex at LNT indicates polycrystalline nature as shown by four weak signals on the left side of the intense peak corresponding to hyperfine resolution of the parallel component. While the intense peak itself corresponds to the perpendicular component of g tensor, $g_{||}$, g , g_{iso} and $A_{||}$ are evaluated as 2.25, 2.07, 2.16 and 145.36 G respectively. These values show that the ligand does not effect much the paramagnetic behaviour of copper complex. These observations suggest tetragonally elongated octahedral environment around copper(II) ion.

The EPR spectrum of Cu(II)·HAHQO complex at LNT has been evaluated to give g_{xx}, g_{yy}, g_{zz} and g_{av} values as 2.063, 2.088, 2.145 and 2.099 respectively. The g tensor of this complex exhibits nearly rhombic symmetry. These observations support square planar geometry of this complex.

Conclusions

Based on the analytical, thermal, conductivity, spectral and magnetic data it has been concluded that the ligands HSHQO, HHAHQO offer different sets of binding sites namely ONN and ONO respectively. All the complexes possess octahedral geometry except Mn(II)·SHQO and Cu(II)·HAHQO which are trigonal bipyramidal and square planar respectively. Further it is interesting to note that the Mn(II) complexes behave differently from others. One is five-coordinate while the other is dimeric which can probably be attributed the difference in the softness of metal ion in comparison with other metal ions. The proposed structures are given in Fig. 2–8. The screening of QD, HQO, HSHQO HHAHQO and metal complexes for antimicrobial activities against *E. coli* and *S. aureus* and for insecticidal properties against housefly are in progress.

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