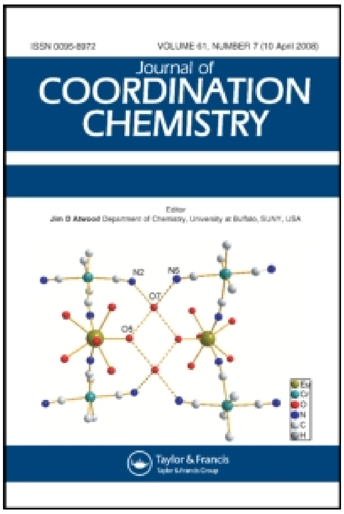

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FIVE- AND SIX-COORDINATE COMPLEXES OF TRIVALENT MANGANESE AND COBALT WITH BENZOYL HYDRAZONES

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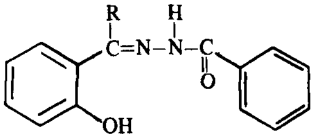
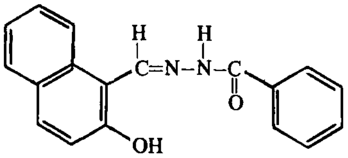
The five- and six-coordinate dimeric manganese(III) and cobalt(III) complexes derived from benzhydrazide and salicylaldehyde(BSH), 0-hydroxyacetophenone(BAH), o-hydroxypropiophenone(BPH), o-hydroxybutyrophenone (BBH) and 2-hydroxy-1-naphthaldehyde(BNH) having the general formulae $[Mn(L)X]_2$ and $[Co(L)(OH)H_2O]_2$ (X = Cl, Br or CH_3COO) are described. These complexes have been characterised by elemental analyses and by conductance, molecular weight, magnetic, electronic and infrared spectral measurements. The complexes of Mn(III) involve phenolic oxygen, while in Co(III) complexes hydroxyl groups are present as bridges between metal atoms as revealed by i.r. spectra. Each unit of dimeric Mn(III) complexes possesses distorted square-pyramidal shape and anions are present on the axial position. The ν(Mn-X) values are consistent with penta-coordinate stereochemistry. These complexes have subnormal magnetic moments (3.40–3.52 BM) explained in terms of antiferromagnetic exchange coupling between two adjacent paramagnetic Mn(III) atoms. The assignments in the electronic spectra of Mn(III) and Co(III) complexes have been made in terms of effective C_{4v} and D_{4h} symmetry, respectively. In both the cases the degree of distortion (DT/DQ) has been calculated by the application of Normalised Spherical Harmonic (NSH) Hamiltonian theory and discussed.

INTRODUCTION

Metal atoms such as trivalent manganese, iron and cobalt have been found to play an important role in green plant photosynthesis and biological system[1-3]. Detailed investigations have been undertaken to find out the exact function of these metal ions in such system[4-6]. Spectromagnetic measurements indicate that these metal ions are bound to enzyme protein systems in the form of chelates. Examples of such proteins which involve manganese(III) are conalbumin[7], transferrin[8], pyruvate carboxylase[9], avimanganin[10], concanvalinA[11] and superoxide dismutase from E. Coli.[12] It has been suggested that multidentate ligands with phenolic oxygen and imine like nitrogen donors can serve as good models for protein bound metal complexes[4]. It has also been observed that manganese(II)[5] and cobalt(II)[13] complexes are converted to dimeric tri- and tetravalent species involving oxo-, peroxo- or hydroxo-bridges between metal atoms. In order to gain more information regarding the structure and stereochemistry of such type of complexes, a comprehensive study of trivalent manganese and cobalt complexes with ligands involving imine-nitrogen, phenolic and enolic-ketonic oxygen as donors has been initiated. Such studies may be useful on two accounts: (i) a knowledge of magnetic and spectral properties of these complexes can solve their structural functional problems in proteins and photosynthesis and (ii) such manganese(III) systems may possess interesting magnetic properties. The structures of the ligands are depicted below:



R = –H(BSH),–CH_3(BAH),–C_2H_5(BPH),–C_3H_7(BBH)



(BNH)

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EXPERIMENTAL

Benzoyl hydrazones were prepared following the method of Struve[14].

Preparation of the Complexes

Following general methods have been adopted to synthesise the complexes.

Manganese(III) complexes Manganese(III) acetate dihydrate and the ligand were taken in 1:1 ratio (0.01 mole each) in 50 ml acetone, refluxed for an hour and concentrated. On cooling, chocolate complexes were obtained which were recrystallised from benzene and dried under vacuum. Yield ~80 percent.

Dark chocolate chloride and bromide complexes of manganese(III) were obtained by adopting the above procedure and adding calculated amounts of LiCl and LiBr in the reaction mixture. Yield ~60 percent.

Cobalt(III) complexes Cobalt(II) chloride hexahydrate (0.01 mole) in 25 ml ethanol was mixed with the ligand (0.01 mole) in 50 ml acetone. The pH of the solution was raised to ~10 by adding 1% ethanolic KOH solution when an initial orange precipitate dissolved to give a brown solution. Air was then passed in the reaction mixture for about three hours resulting in dark brown complexes. The complexes were recrystallised from benzene and dried under vacuum. Yield ~70 percent.

Manganese(III) and Cobalt(III) complexes were also synthesised by taking 1:2 and 2:1 metal to ligand stoichiometry and in each case the complexes obtained were similar to those prepared by taking 1:1 metal to ligand ratio. However, it may be pointed out that difficulties were encountered in the isolation of the complexes of ligands having bulkier R group. Probably, bulkier R group present on the carbon atom forming azomethine linkage hindered the bonding between metal atom and unsaturated nitrogen of (C=N) group.

Analyses and apparatus A Toshniwal conductivity bridge (CL01/01) with a dip-type cell was used to measure the conductivity of the complexes at room temperature. The electronic spectra were recorded in dimethylformamide on Beckman DMR-21, infrared on Perkin Elmer-621 (in KBr pellets) and far i.r on Beckman IR-12 spectrophotometers (in nujol-mull). Magnetic measurements on powder form of the complexes were made on a Gouy balance using $[HgCo(CNS)_4]$ as calibrant. Cobalt(III) and manganese(III) were estimated by EDTA titration using Eriochrome Black T as indicator. It was ensured that Mn(III) was converted into Mn(II) by repeatedly treating the complexes with concentrated nitric and sulphuric acids. Halides were estimated by Volhard's method.

RESULTS AND DISCUSSION

The elemental analyses (Table I) indicate that all complexes have 1:1 metal to ligand stoichiometry. The complexes can be represented by the formulae [Mn(L)X], X = CH_3COO, Cl and Br and $[Co(L)(OH)H_2O]$. The electrical conductance measurements in nitromethane and dimethylformamide are consistent with the non-electrolytic nature of the complexes. The molecular weights determined cryoscopically in benzene are not compatible with the above formulae of the complexes. Instead, the ratio of calculated and observed molecular weights vary from 1:1.95 to 1:2.10. The observed molecular weights may be inferred as originating from the dimerisation of the complexes.

Infrared spectra The strong absorptions at 3200–3250 and 2700–2775 cm^{-1} in the infrared spectra of the ligands are assigned to ν(OH) vibrations involving hydrogen bonding[15]. The bands in the regions 1660–1675, 1515, 1250, 650 and 495 cm^{-1} appear to be due to amide I(νC=O), amide II(νCN + δNH), amide III(δNH), amide IV (C=O in-plane deformation) and amide VI (C=O out-of-plane deformation) vibrations, respectively, and suggest that the ligands are present in the keto-form.[16,17] The vibrations between 1615–1625 cm^{-1} are assigned to ν(C=N) of azomethine group.

Conspicuous changes are found in the spectra of the complexes which do not show characteristic bands of amide and amino groups suggesting that the ligands are bound in the enolic form. The downward shift (15–20 cm^{-1}) of ν(C=N) mode indicates that the nitrogen of the azomethine group is coordinated to the metal atom. A new band appearing ~1595 cm^{-1} seems to have its origin in the stretching vibration mode of the conjugate $>C=N-N=C<$ grouping analogous to that of azines[18], suggesting the participation of enolic oxygen. The disappearance of the bands at 3200–3250 and 2700–2775 cm^{-1} supports the involvement of phenolic oxygen in coordination through deprotonation. The bands

TABLE I
Molecular weight and analytical data of manganese(III) and cobalt(III) complexes (X=Cl, Br).

Compound	Molecular weight		Analytical data									
			Found%					Calculated%				
	Calcd.	Found	M	C	H	N	X	M	C	H	N	X
[$Mn(C_{14}H_{10}N_2O_2)CH_3COO$]	352.2	692.0	15.72	54.90	3.74	8.02	–	15.59	54.56	3.71	7.95	–
[$Mn(C_{15}H_{12}N_2O_2)CH_3COO$]	366.2	757.6	14.95	55.99	4.07	7.69	–	15.00	55.75	4.12	7.64	–
[$Mn(C_{16}H_{14}N_2O_2)CH_3COO$]	380.2	771.8	14.30	56.61	4.55	7.30	–	14.44	56.85	4.50	7.36	–
[$Mn(C_{17}H_{16}N_2O_2)CH_3COO$]	394.2	768.0	14.01	58.20	4.91	7.01	–	13.93	57.88	4.86	7.10	–
[$Mn(C_{18}H_{12}N_2O_2)CH_3COO$]	402.2	843.4	13.56	59.39	3.75	6.86	–	13.65	59.72	3.76	6.96	–
[$Mn(C_{14}H_{10}N_2O_2)Cl$]	328.6	687.1	16.74	50.99	3.09	8.41	10.93	16.71	51.16	3.06	8.52	10.79
[$Mn(C_{18}H_{12}N_2O_2)Cl$]	378.6	750.7	14.59	57.21	3.21	7.35	9.51	14.51	57.10	3.19	7.39	9.36
[$Mn(C_{14}H_{10}N_2O_2)Br$]	373.0	742.2	14.61	45.38	2.75	7.45	21.25	14.72	45.07	2.70	7.51	21.42
[$Mn(C_{18}H_{12}N_2O_2)Br$]	423.1	859.3	13.35	48.98	3.80	6.83	19.32	13.23	49.19	3.88	6.75	19.25
[$Co(C_{14}H_{10}N_2O_2)(OH)(H_2O)$]	332.2	697.6	17.90	50.49	3.99	8.50	–	17.74	50.61	3.94	8.42	–
[$Co(C_{15}H_{12}N_2O_2)(OH)(H_2O)$]	346.2	695.8	16.89	51.75	4.30	7.99	–	17.02	52.03	4.36	8.08	–
[$Co(C_{16}H_{14}N_2O_2)(OH)(H_2O)$]	360.2	706.0	16.42	53.59	4.84	7.85	–	16.36	53.34	4.75	7.77	–
[$Co(C_{17}H_{16}N_2O_2)(OH)(H_2O)$]	374.2	767.1	17.70	54.79	4.99	7.60	–	15.75	54.56	5.11	7.48	–
[$Co(C_{18}H_{12}N_2O_2)(OH)(H_2O)$]	382.2	766.3	15.50	56.92	3.92	7.21	–	15.42	56.56	3.95	7.32	–

appearing ~485, 460 and 370 cm^{-1} may be assigned to ν(Mn–O) (phenolic), ν(Mn–N) and ν(Mn–O) (enolic) vibrations[19–21], respectively. Similar vibrations in the cobalt complexes are observed ~495, 475 and 380 cm^{-1}, respectively.

In the spectra of the ligands, bands observed around 1520 and 1280 cm^{-1} can be assigned to C–O stretching[15] and bending vibrations, respectively. On complexation, these bands exhibit an upward shift of 10–25 cm^{-1} in manganese(III), whereas in case of cobalt(III) the position of these bands remains unchanged or shows a slight decrease in frequency. This upward shift in the two bands is consistent with the bi- or polymeric structure[22,23] of manganese(III) complexes involving bridged phenolic oxygen. Further, the appearance of a new band at 620–630 cm^{-1} characteristic of $\mathrm{Mn}^{3+}\begin{smallmatrix}\mathrm{O}\\ \langle\;\rangle\\ \mathrm{O}\end{smallmatrix}\mathrm{Mn}^{+3}$ ring vibrations[24] confirms their dimeric nature. The cobalt(III) complexes show a strong band around 1150 cm^{-1} due to Co–OH bending and another new band at 880 cm^{-1} assignable to the rocking modes of coordinated water. These indicate that hydroxyl group is acting as bridges between two cobalt atoms, thus making the complexes binuclear.[13, 15, 25]

In the acetato complex of manganese(III), two bands are observed ~1640 and 1390 cm^{-1} which may be assigned to antisymmetric and symmetric (COO) stretching vibrations. These values indicate that the acetate group is coordinated to the metal ion and that metal-oxygen bond so formed is moderately covalent[15].

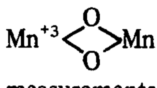
Some additional bands are observed in the ranges 330–335 and 260–265 cm^{-1} in the spectra of chloride and bromide complexes of manganese(III) which may be assigned to ν(Mn–Cl) and ν(Mn–Br) stretching vibrations, respectively. The metal oxygen stretching vibration also occurs around 300 cm^{-1} and thus it appears that these vibrations are not "pure" and have substantial contribution from ν(Mn–O) vibrations. However, the value of ν(Mn–Br)/ν(Mn–Cl) comes out to be 0.78 which is consistent with the expected ratio reported by Nakamoto[15]. Another point of interest is that these values observed for ν(Mn–Cl) and ν(Mn–Br) have magnitude intermediate to those observed for six- and four-coordinate complexes.[26]. This may be interpreted in terms of penta-coordinate geometry of these complexes. Similarly, the acetato complexes show a broad band of medium intensity around 230 cm^{-1} which appear to have its origin in ($Mn-OCOCH_3$) stretching vibration.

TABLE II

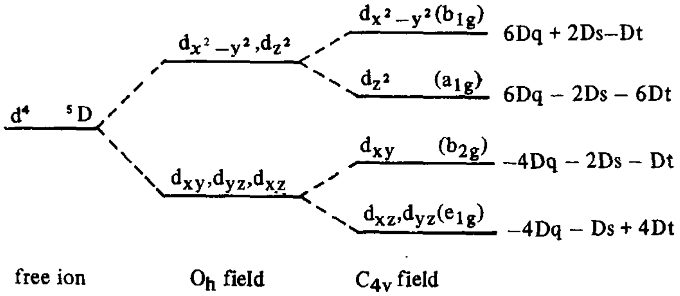
Magnetic and electronic spectral data (cm^{-1}) of five-coordinate trivalent manganese complexes (ϵ in parenthesis)

Compound	$\mu_{eff.}$ B.M. 303°K	$d_{z^2} \rightarrow d_{x^2-y^2}$	$d_{xy} \rightarrow d_{x^2-y^2}$	$d_{xz}d_{yz} \rightarrow d_{x^2-y^2}$	Charge Transfer	Dq^{xy}	Dq^z	Ds	Dt	DQ	DS	DT	DT/DQ	DQ^{xy}	DQ^z
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
$[Mn(BSH)OAc]_2$	3.52	12050 (165)	15870 (320)	20830 (1320)	22470 (12300) 28570 (19250) 35100 (35200)	1587	772	2430	466	36175	−17010	6320	0.174	43640	21215
$[Mn(BAH)OAc]_2$	3.47	12320 (200)	15600 (310)	21800 (1280)	23720 (12900) 29210 (19000) 37100 (35600)	1560	951	2646	348	37320	−18520	4720	0.127	42905	26150
$[Mn(BPH)OAc]_2$	3.45	11980 (190)	15520 (350)	21790 (1350)	23620 (11750) 28810 (18800) 36400 (34850)	1552	1010	2607	310	37710	−18250	4200	0.111	42680	27770
$[Mn(BBH)OAc]_2$	3.40	12050 (150)	15460 (300)	21610 (1290)	23380 (11400) 29400 (18100) 36700 (34550)	1546	969	2600	330	37220	−18200	4475	0.120	42515	26630
$[Mn(BNH)OAc]_2$	3.48	12420 (175)	15440 (375)	21670 (1325)	23810 (12500) 29850 (18750) 37430 (35550)	1544	928	2664	352	36805	−18650	4770	0.130	42450	24515
$[Mn(BSH)Cl]_2$	3.50	12120 (150)	15380 (300)	21050 (1305)	23260 (11900) 28990 (20000) 37700 (34700)	1538	850	2541	390	36035	−17790	5290	0.146	42295	23515
$[Mn(BNH)Cl]_2$	3.48	12260 (185)	15300 (340)	21520 (1300)	23200 (11550) 29400 (19700) 35720 (35100)	1530	935	2640	340	36625	−18480	4610	0.126	42080	25715
$[Mn(BSH)Br]_2$	3.50	12140 (180)	15380 (350)	21730 (1335)	23810 (11600) 29900 (19900) 35200 (34450)	1538	954	2641	334	36945	−18490	4525	0.122	42300	26235
$[Mn(BNH)Br]_2$	3.42	12230 (190)	15330 (320)	21470 (1345)	23490 (12500) 29780 (18050) 35900 (35150)	1533	928	2624	346	36600	−18370	4690	0.128	42150	25500

Magnetic and electronic spectral studies The room temperature values of magnetic moment for manganese(III) complexes lie in the range 3.40–3.52 BM. These values of $\mu_{eff.}$ are appreciably lower than those exhibited by high-spin five- or six-coordinate trivalent manganese complexes[26, 27]. The operation of antiferromagnetic spin-exchange coupling between neighbouring manganese(III) ions appears to be the main reason for the subnormal values of the magnetic moments. Several other dimeric manganese(III) complexes of Schiff bases[5, 26] are known to possess reduced magnetic moments and in one such case[28] the dimeric nature with


$Mn^{+3}\langle O_2 \rangle Mn^{+3}$ unit has been established with X-ray measurements.

The electronic spectra of the complexes have been recorded in dimethylformamide in the range 200–2500 mμ. The spectra show bands in the regions 11890–12420, 15300–15870, 20830–21800, 22470–23810, 28570–29900 and 35100–37700 cm^{-1}. The bands up to 21800 cm^{-1} appear to have their origin in d-d transitions while others having higher energy are charge-transfer. The molecular model of these dimeric complexes favour square-pyramidal shape having effective symmetry around the metal ion as C_{4v}. The following energy level diagram [29, 30] for a d^4 system in such a field predicts three d-d transitions.



Thus, the observed bands around 12000, 15500 and 21500 cm^{-1} may be assigned to $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$ transitions in the order of increasing energy.[4, 5, 31] The splitting diagram shows that the transition $d_{xy} \rightarrow d_{x^2-y^2}$ is the direct measure of 10Dq. It may be pointed out that with this set of chromophore a trigonal-bipyramidal configuration is also possible as there is small energy difference between this and square-pyramidal configuration. However, in the present complexes the latter configuration is preferred with bulky ligands[32]

The bands appearing above 21800 cm^{-1} are charge-transfer in nature. The absorption around 23000 and 29000 cm^{-1} can be assigned to metal-to-ligand (azomethine linkage) charge-transfers i.e. $d_{z^2} \rightarrow \pi^*$, $d_{xz}, d_{yz} \rightarrow \pi^*$; $d_{xy} \rightarrow \pi^*$ is probably buried between these two transitions. The intense higher energy band observed around 36500 cm^{-1} may be because of the ligand $\pi \rightarrow \pi^*$ transition of the phenolic group[33]. These charge transfer bands are broad and in some cases appear as shoulders, but they do not look to be anion dependent as no regular pattern is observed in their energies on going from acetate to chloride or bromide. There is no detectable effect of the change of R group present on the azomethine carbon atom in the electronic spectra of the complexes.

In fact, the symmetry of the complexes is not idealised C_{4v}, but is lower than that because of the non-equivalence of the donor atoms. Thus the presence of the lower symmetry elements and consequently the distortion of the idealised symmetry appears to be a reasonable feature of these complexes. The amount of the tetragonal distortion can be calculated by the application of newly developed theory of Normalized Spherical Harmonic (NSH) Hamiltonian.[34, 35].

The various ligand field parameters are designated as DQ, DS and DT in NSH theory. These parameters are fully capitalized to relate them to the corresponding crystal field parameters, yet emphasize their distinction. The NSH Hamiltonian parameters and those of classical Hamiltonian are related as:

$$DS = -7Ds$$
$$DT = (7\sqrt{15}/2)Dt$$
$$DQ = (6\sqrt{21})Dq - (7\sqrt{21}/2)Dt.$$

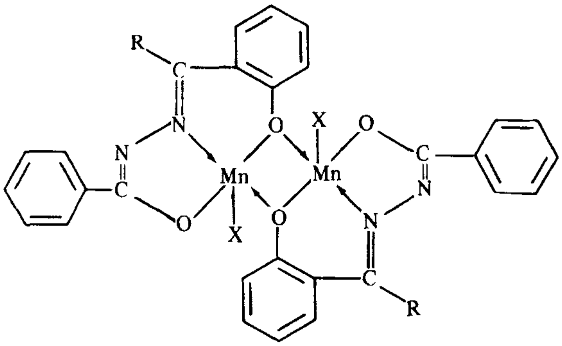
There are several advantages of the NSH Hamiltonian theory viz., (a) the theory takes into account an off diagonal contribution to Dt, (b) DQ is a measure of the average ligand field experienced by the metal ion unlike the classical Dq which is the measure of the in-plane ligand field and (c) the parameters of NSH theory are independent of the coordinate system used for calculations and may be compared with the crystal field or angular overlap parameters to determine restrictions on these values. The magnitude of the ratio DT/DQ is a useful measure of the degree of tetragonal distortion and in certain circumstances, it indicates that in a five-coordinate square-pyramidal complex, the metal is out of the molecular plane.

Various ligand field and NSH parameters are calculated (Table II). The degree of distortion calculated in terms of DT/DQ comes out to be 0.111-0.175. These values are appreciably lower than the theoretical limiting value of 0.4226, a value calculated for square-planar complexes. The small degree of distortion indicates that the manganese(III) complexes are weakly distorted. The parameters DQ^{xy} and DQ^z have also been calculated with the help of following equations:

$$DQ = \left(\frac{1}{6}\right)(4DQ^{xy} + 2DQ^z)$$

$$DT = \left(\frac{\sqrt{5}}{\sqrt{7}}\right)(DQ^{xy} - DQ).$$

However, it may be pointed out that these parameters have artificial significance[35], for DQ itself is a measure of average ligand field strength.



The room temperature magnetic moments show that cobalt(III) complexes are spin-paired and exhibit only a small paramagnetism of the temperature independent type. This supports the conclusion that the compounds contain cobalt in the 3^+ oxidation state.

The electronic spectra recorded in dimethylformamide show bands in the regions 16550–17200, 22520–23650, 25580–26000, 29000–30000 and 36800–37500 cm^{-1}.

The electronic spectra can be interpreted to establish the configuration of cis-or-trans isomers of pseudooctahedral cobalt(III). For an octahedral complex, two d-d bands corresponding to ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions are expected.[36] In idealised O_h symmetry, the separation between the above two transitions is about 7000–10000 cm^{-1} and if the separation is <7000 cm^{-1}, the presence of lower symmetry elements is expected. Lowering of octahedral symmetry ($O_h \rightarrow D_{4h}$) causes ${}^1T_{1g}$state to split into A_{2g} and E_g states[37]. The lower symmetry cobalt(III) complexes usually conform either to C_{2v} (cis-) or D_{4h} (trans-) symmetry. The bands observed for the present complexes are consistent with the pseudooctahedral (tetragonal) nature, as separation between first and second bands is ~6000 cm^{-1}. Thus the bands appearing around 17000, 22500 and 25750 cm^{-1} may be assigned to ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions in the order of increasing energy by assuming the effective field around cobalt ion as D_{4h}. The other two bands are charge-transfer, one occurring ~29000 cm^{-1} is probably due to metal-to-ligand (azomethine linkage) and the higher energy band ~37000 cm^{-1} may be due to $\pi \rightarrow \pi^*$ transition of phenolic group within the ligand.[33]

Wentworth and Piper[37] advanced the mathematical equations, $\nu A({}^1A_{1g} \rightarrow {}^1A_{2g}) = 10Dq^{xy} - C$, $Dt = \frac{4}{35}(10Dq^{xy} - \nu_E - C)$ and $Dq^z = Dq^{xy} - \frac{7}{4}Dt$, where $\nu_E = {}^1A_{1g} \rightarrow {}^1E_g$, C is the interelectronic repulsion term (3800 cm^{-1}), Dt is a measure of splitting of T_{1g} state (O_h symmetry) into two components A_{2g} and E_g. Dq^{xy} and Dq^z are in-plane and out-of-plane field strengths, respectively to rationalise the spectra of tetragonally distorted octahedral cobalt(III) complexes. The values of various ligand field parameters (Table III) are comparable to those observed for cobalt(III) complexes of ligands having similar chromophores[38]

The degree of distortion of these complexes has also been calculated in terms of DT/DQ which lie in the range 0.150–0.164. These values are not appreciably higher and indicate that cobalt complexes are moderately distorted.

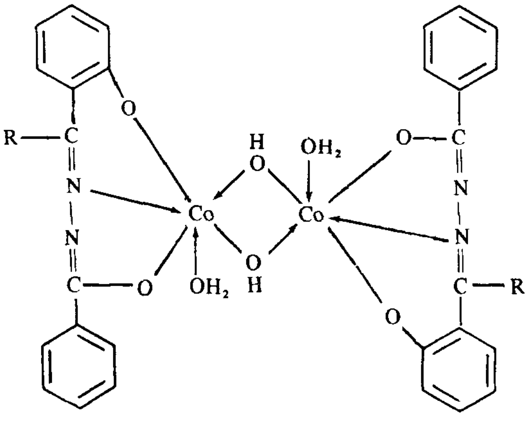


TABLE III

Electronic spectral data (cm^{-1}) of six-coordinate trivalent cobalt complexes (ϵ in parenthesis)

Compound	$^1A_{1g} \rightarrow$ ^1E_g	$^1A_{2g}$	$^1T_{2g}, {}^1E_g^b$	Charge transfer	Dt	Dq^{xy}	Dq^z	DT	DQ	DT/DQ	DQ^{xy}	DQ^z
$[Co(BSH)(OH)(H_2O)]_2$	16550 (95)	22520 (130)	25720 (2050)	29000 (~22000) 37500 (~17000)	682	2632	1438	9241	61435	0.150	72365	39255
$[Co(BAH)(OH)(H_2O)]_2$	16620 (100)	22850 (127)	25810 (2110)	29250 (~21000) 37000 (~14000)	712	2665	1419	9647	61862	0.156	73370	38720
$[Co(BPH)(OH)(H_2O)]_2$	17200 (75)	23550 (110)	25900 (2200)	29800 (~26000) 36800 (~12000)	725	2735	1467	9823	63578	0.154	75200	41020
$[Co(BBH)(OH)(H_2O)]_2$	16850 (80)	23000 (115)	25580 (2500)	29100 (~23000) 37270 (~15000)	702	2680	1451	9512	62434	0.152	73695	39635
$[Co(BNH)(OH)(H_2O)]_2$	17000 (90)	23650 (125)	25850 (2430)	29200 (~20000) 37100 (~18000)	760	2745	1415	10298	63292	0.164	75470	38570

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