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BINUCLEAR CHROMIUM(III), MANGANESE(III), IRON(III) AND COBALT(III) COMPLEXES BRIDGED BY DIAMINOPYRIDINE

D. P. SINGH*

Department of Chemistry, Regional Engineering College, Kurukshetra-132 119, India

and

V. B. RANA

Department of Chemistry, Meerut College, Meerut-250 001, India

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Abstract—Trivalent chromium, manganese, iron and bivalent cobalt salts react with 2,6-diaminopyridine and acetylacetone to give complexes of the type [M($C_{15}H_{17}N_3O_2$)X] [where X = Cl, Br, NO_3 or NCS for M = chromium(III) and iron(III); X = Cl, Br, OAc or NCS for manganese(III)]. Conductance measurements show the complexes to be non-electrolytes. Molecular weights determined cryoscopically suggest the dimeric nature of these complexes. Magnetic measurements above 85 K reveal the presence of some anti-ferromagnetic exchange via 2,6-diaminopyridine moieties. The complexes are dimeric five-coordinate square-pyramidal with 2,6-diaminopyridine residues acting as bridges. The electronic spectra are interpreted in terms of the normalized spherical harmonic Hamiltonian theory and the DT/DQ values which indicate that chromium complexes are slightly distorted, whereas those of manganese are severely distorted.

Schiff bases derived from aromatic diamines and mono- or dicarbonyl compounds are multidentate ligands which can act in a variety of ways.[1,2] The oxygen or diamine groups may bridge two metal atoms and thus may give rise to some unusual species.[3] This has led to the synthesis and characterization of metal complexes with unusual structural and magnetic properties.[2,4] Prompted by this, we have already reported binuclear divalent manganese, iron, cobalt, nickel, copper, palladium and platinum complexes of the ligands bis-acetylacetone-*m*-phenylenediamine ($Acac_2pda$) and bisacetylacetone-2,6-diaminopyridine ($Acac_2dap$)[5,6] and binuclear complexes of trivalent chromium, manganese, iron and cobalt with ligand bisacetyl-acetone-*m*-phenylenediamine ($Acac_2pda$).[7] The present paper deals with binuclear square-pyramidal complexes of trivalent chromium, manganese, iron and cobalt with ligands derived from 2,6-diaminopyridine and acetylacetone.

EXPERIMENTAL

2,6-Diaminopyridine and acetylacetone were obtained from Koch-Light and BDH, England, respectively. All other chemicals used were of AnalaR grade.

Preparation of metal complexes with bis-acetylacetone-2,6-diaminopyridine

To a boiling mixture of acetylacetone (0.04 mol) and 2,6-diaminopyridine (0.02 mol) in methanol (100 cm^3) was added a trivalent (except Co) metal salt (chloride or nitrate) (0.02 mol) solution in methanol (50 cm^3). The resulting dark reaction mixture was heated under reflux for 8 h on a waterbath,

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*Author to whom correspondence should be addressed.

then concentrated to half its volume and set aside for 3 days. The dark solid which separated was extracted repeatedly with acetone and finally recrystallized from methanol and dried *in vacuo*; yield 65%. The bromo- and thiocyanato-salts were prepared by the metathesis process and manganese(III) acetate was prepared by Christensens' method.[8]

Cobalt complex

A mixture of 2,6-diaminopyridine (0.02 mol) in methanol (50 cm^3) and acetylacetone (0.04 mol) in methanol (50 cm^3) was heated under reflux for 4 h and then a methanolic (50 cm^3) solution of cobalt(II) chloride (0.02 mol) was added. Air was passed through for 18 h and the resulting violet solution gave a brown precipitate which was filtered off, washed with ethanol, acetone, ether and dried *in vacuo*; yield 60%.

All the complexes are soluble in DMF and DMSO, but insoluble in organic solvents and water, except those of iron which are water soluble.

The analytical and physical measurements were carried out as previously described.[9]

RESULTS AND DISCUSSION

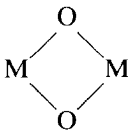
The analytical results (Table 1) show that these complexes can be formulated as [M($C_{15}H_{17}N_3O_2$)X], where (X = Cl,Br,NO_3 or NCS for M = Cr^{III} or Fe^{III}; X = Cl,Br,OAc or NCS for Mn^{III}; and X = OH for Co^{III}). The iron(III) complexes in water, and all the other complexes in DMF, are non-electrolytes.[10] The cryoscopic molecular weight of the iron complexes in water, showed them to be binuclear.

IR spectra

The IR spectra of free ligands show a broad band in the *ca* 3200 cm^{-1} region, which may be due to OH or NH groups, which disappear in the complexes. There is no absorption in the *ca* 1700 cm^{-1} region, indicating the absence of any free carbonyl group in the ligands or in metal chelates. It is also clear that the six-membered rings containing the hydrogen bonds are greatly stabilized by conjugation, as is the case with β-diketones and salicylaldehyde.[11] The strong absorption band at *ca* 1630–1610 cm^{-1} in the free ligand can be assigned to $\nu(>C{=}O)$ in the hydrogen-bonded ring system. The other strong absorption at *ca* 1590–1580 cm^{-1} in the ligand, accompanied by a weaker absorption at *ca* 1550–1560 cm^{-1}, can be assigned to $\nu(C{=}C)$ stretching vibrations in the hydrogen-bonded ring. The bands at *ca* 1590–1580 cm^{-1} are shifted to slightly higher frequencies upon chelation, while those at *ca* 1550–1560 cm^{-1} shift to a lesser extent. The bands at *ca* 1450–1460 cm^{-1} in the free ligand (assigned to NH deformation) are not observed in the spectra of the metal chelates. Another band at *ca* 1150 cm^{-1} is assigned to $\nu(C{-}O)$ stretching vibrations and is shifted to a lower region by metal chelation. This shift may be due to an increase of mass of metals attached to oxygen, as well as to a weakening of the (C—O) linkage.[12] The other bands at *ca* 1570–1580, 1460–1490 and 1430–1445 cm^{-1} may be assigned to $\nu(C{=}O)$ and $\nu(C{=}N)$ vibrational modes of the pyridine ring[13,14] and do not exhibit much change in their position or intensity in the spectra of its complexes and thus rule out the possibility of pyridine nitrogen coordination.

Magnetic properties and electronic spectral studies

The magnetic moments of chromium, manganese and iron complexes lie in the 4.20–4.35, 4.88–4.94 and 5.80–5.86 B.M. ranges, respectively, at room temperature and are close to the predicted high-spin values for these metal ions.[15] The cobalt(III) complex is diamagnetic.

The magnetic susceptibilities of the chloro-complexes of chromium and iron were measured down to 80 K and the effective magnetic moment per metal ion was found to vary in the 4.20–3.86 (Cr) and 5.80–4.52 B.M. (Fe) ranges. In the iron complexes, μ_{eff} is almost constant above 150 K with a gradual decrease between 150 and 80 K. The Curie–Weiss law is obeyed with a negative θ. This reflects intramolecular antiferromagnetic interactions at lower temperature.[16] However, there are no indications of the presence of any antiferromagnetic interactions at room temperature. Probably 2,6-diaminopyridine residues act as bridges in these complexes. Bridging through oxygen atoms can be ruled out since no band characteristics of  at *ca* 750–800 cm^{-1} are seen in the IR spectra.[17] Such complexes have not been studied, whereas bridging complexes formed by *m*-phenylenediamine and salicylaldehyde having a similar structure were established by X-ray crystallography.[12]

The electronic spectra of the chromium complexes exhibit bands at *ca* 8900–9250, 12 850–13 250, 17 850–18 220, 27 200–27 920 and 35 550

Table 1. Analytical data of trivalent chromium, manganese, iron and cobalt complexes[a]

Complex	Colour	Found (Calc.)% M	C	H	N	Halogen
1, $[Cr(C_{15}H_{17}N_3O_2)Cl]$	Light brown	14.4 (14.5)	50.6 (50.2)	4.9 (4.7)	11.3 (11.7)	9.5 (9.9)
2, $[Cr(C_{15}H_{17}N_3O_2)Br]$	Light brown	12.8 (12.9)	4.5 (44.6)	4.2 (4.2)	10.3 (10.4)	19.7 (19.8)
3, $[Cr(C_{15}H_{17}N_3O_2)NO_3]$	Yellowish-brown	13.6 (13.5)	46.5 (46.7)	4.3 (4.4)	14.4 (14.5)	16.0 (16.1)
4, $[Cr(C_{15}H_{17}N_3O_2)NCS]$	Brown	13.4 (13.6)	47.1 (47.2)	4.3 (4.4)	14.7 (14.6)	—
5, $[Mn(C_{15}H_{17}N_3O_2)Cl]$	Reddish-brown	15.1 (15.2)	49.8 (49.7)	4.6 (4.7)	11.5 (11.6)	9.8 (9.8)
6, $[Mn(C_{15}H_{17}N_3O_2)Br]$	Reddish-brown	13.4 (13.5)	44.4 (44.3)	4.2 (4.1)	10.4 (10.3)	19.3 (19.7)
7, $[Mn(C_{15}H_{17}N_3O_2)OAc]$	Brown	14.1 (14.2)	56.0 (56.1)	5.2 (5.1)	10.8 (10.9)	—
8, $[Mn(C_{15}H_{17}N_3O_2)NCS]$	Dark brown	14.2 (14.3)	50.7 (50.0)	4.3 (4.4)	14.3 (14.5)	—
9, $[Fe(C_{15}H_{17}N_3O_2)Cl]$	Reddish-brown	15.3 (15.4)	49.5 (49.6)	4.6 (4.6)	11.5 (11.6)	9.7 (9.8)
10, $[Fe(C_{15}H_{17}N_3O_2)Br]$	Reddish-brown	13.6 (13.7)	44.3 (44.2)	4.2 (4.1)	10.3 (10.3)	19.5 (19.6)
11, $[Fe(C_{15}H_{17}N_3O_2)NO_3]$	Dark red	14.4 (14.3)	46.3 (46.2)	4.6 (4.3)	14.4 (14.3)	14.6 (14.6)
12, $[Fe(C_{15}H_{17}N_3O_2)NCS]$	Dark brown	14.5 (14.5)	49.8 (49.8)	4.4 (4.4)	14.4 (14.5)	—
13, $[Co(C_{15}H_{20}N_3O_4)]$	Light green	16.0 (16.1)	49.2 (49.3)	5.5 (5.4)	17.6 (17.5)	—

[a] Calculated values are given in parentheses.

cm^{-1}. These spectral bands cannot be interpreted in terms of a four- or six-coordinate environment around the metal atom. However, the spectra can well be compared with five-coordinate chromium(III) complexes, whose structures have been established by X-ray measurements.[18] Keeping in view the analytical data which indicate one anion per metal atom and the non-electrolytic nature of these complexes, it appears that these complexes are five-coordinate square-pyramidal. Besides, the tetradentate nature of a single molecule of Acac$_2$dap offers a planar arrangement and an anion being present on the axial position makes the total environment square-pyramidal. Assuming the symmetry of the molecule[9] as C_{4v}, various spectral bands can be assigned: ${}^4B_1 \rightarrow {}^4E^a$, ${}^4B_1 \rightarrow {}^4B_2$, ${}^4B_1 \rightarrow {}^4A_2$ and ${}^4B_1 \rightarrow {}^4E^b$. Employing the energy level equations for C_{4v} molecules, the radial field parameters, Ds and Dt, were calculated and in turn used to calculate the normalized spherical harmonic Hamiltonian ligand field parameters DQ, DS and DT.[19] The values are given in Table 2. The DT/DQ values show that these complexes are moderately distorted.

The electronic spectra of the manganese complexes exhibit three *d*–*d* bands at *ca* 12 400–12 850, 16 050–19 750, 20 500–20 850 and 35 000–36 000 cm^{-1}, respectively. The higher energy bands at *ca* 35 000–36 000 cm^{-1} may be due to charge-transfer transitions. The spectra, however, rule out the possibility of four- or six-coordinate geometry, and resemble those reported four five-coordinate square-pyramidal manganese porphyrins.[9] This view is further supported by the presence of the broad ligand field band at *ca* 20 500 cm^{-1} diagnostic of C_{4v} symmetry, thus the bands may be assigned as follows: ${}^5B_1 \rightarrow {}^5A_1$, ${}^5B_1 \rightarrow {}^5B_2$ and ${}^5B_1 \rightarrow {}^5E$, respectively. Alternatively, the band assignment in single electron transitions may be made as: $d_{z^2} \rightarrow d_{x^2-y^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively, in order of increasing energy.[20] However, the complexes may not conform to idealized C_{4v} symmetry because of the presence of donor atoms of unequal size and strength. Using the

Table 2. Electronic and magnetic spectral data of trivalent chromium, manganese and cobalt complexes

Complexes	Spectral bands (cm^{-1})	Dq^{xy} (cm^{-1})	Dq^{z} (cm^{-1})	Ds ($-$) (cm^{-1})	Dt (cm^{-1})	DS ($-$) (cm^{-1})	DT (cm^{-1})	DQ (cm^{-1})	DT/DQ (cm^{-1})	DQ^{z} (cm^{-1})	DT/DQ	μ_{eff}(B.M.) at 300 K
1, $[\mathrm{Cr(Acac_2dap)Cl}]_2$	8900, 12 850, 17 850, 27 200	1285	495	1464	451	10 248	6113	28 098	35 332	13 630	0.21	4.35
2, $[\mathrm{Cr(Acac_2dap)Br}]_2$	9050, 13 050, 17 950, 27 550	1305	505	1504	457	10 528	6194	28 552	35 882	13 892	0.21	4.30
3, $[\mathrm{Cr(Acac_2dap)NO_3}]_2$	9175, 13 150 18 150, 27 800	1315	520	1513	454	10 591	6154	28 875	36 157	14 310	0.22	4.34
4, $[\mathrm{Cr(Acac_2dap)NCS}]_2$	9250, 13 250, 18 220, 27 920	1325	525	1521	457	10 647	6194	29 101	36 431	14 441	0.22	4.28
5, $[\mathrm{Mn(Acac_2dap)Cl}]_2$	12 650, 35 800, 18 600, 27 700	1860	383	2107	844	14 749	1440	37 605	51 143	10 529	0.30	4.90
6, $[\mathrm{Mn(Acac_2dap)Br}]_2$	12 700, 35 650, 19 750, 20 750	1975	270	1957	974	13 699	13 203	38 682	54 306	7433	0.34	4.94
7, $[\mathrm{Mn(Acac_2dap)OAc}]_2$	12 600, 35 720, 18 650, 20 500	1865	346	2064	868	14 448	11 766	37 358	51 282	9510	0.51	4.92
8, $[\mathrm{Mn(Acac_2dap)NCS}]_2$	12 550, 35 900, 17 650, 20 700	1765	492	2228	727	15 596	9854	36 869	48 530	13 546	0.27	4.88
9, $[\mathrm{Co(Acac_2dap)(OH)H_2O}]_2$	25 050, 35 550, 16 250	2505	1506	—	571	—	7740	59 718	68 877	41 399	0.129	Diamagnetic

energy level sequence for C_{4v} molecules, the values of classical and NSH parameters were calculated. The values of DT/DQ indicate that these complexes are severely distorted.

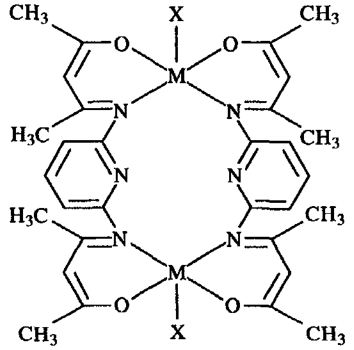
The electronic spectra of iron(III) complexes show various bands at *ca* 9800–10 000, 15 400–15 600 and 27 000–27 200 cm^{-1} and do not suggest either octahedral or tetrahedral geometry around the metal atom. The spectral bands for these complexes are well within the range reported for square-pyramidal five-coordinate iron(III) complexes.[21] Assuming C_{4v} symmetry of these complexes, some bands can be assigned as: $d_{xy} \rightarrow d_{xz}$, d_{yz} and $d_{xy} \rightarrow d_{z^2}$. Any attempt to make accurate assignments is difficult due to the likelihood of interactions of the metal–ligand π-bond systems lifting the degeneracy of the d_{xz}, d_{yz} pair.

The spectrum of the cobalt(III) complex shows various bands in the regions *ca* 15,900–16,250, 21,500–21,750 and 25,500–25,780 and 35,500 cm^{-1}. The spectrum is typical of pseudo-octahedral complexes of trivalent cobalt and resemble those reported earlier.[22] The first two bands are due to the splitting of a one-spin allowed band since octahedral cobalt(III) complexes show only two bands in the visible and near-IR region. Therefore, the spectrum can easily be interpreted in terms of D_{4h} symmetry. Various band assignments can be made: ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1A_{1g} \rightarrow {}^1A_{2g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$, in order of increasing energy. The values of various ligand field parameters, Ds, Dt and Dq, and NSH parameters, DS, DT and DQ, are mentioned in Table 2. The DT/DQ value, which represents the amount of distortion, indicates that this complex is moderately distorted. The other band at *ca* 35 500 cm^{-1} is due to a charge-transfer, metal-to-ligand (azomethine) transition.[23] The presence of the sixth ligand in the cobalt complex is shown by IR spectra and analytical data. The IR spectrum indicates the presence of a water molecule in the coordination sphere.

Far-IR spectra

The far-IR spectra of the complexes show a series of strong to medium bands appearing in the *ca* 450–480 cm^{-1} region. The various bands appearing at *ca* 455–460, 465–470, 470–475 and 450–455 cm^{-1} have been assigned to ν(Cr—N), ν(Mn—N), ν(Fe—N) and ν(Co—N) metal–nitrogen (azomethine) vibrational modes, respectively, and are well within the range reported for five-coordinate complexes, but for ν(Co—N) which is comparatively in a lower range pointing towards six-coordination. The far-IR spectra of these complexes also exhibit new bands in the *ca* 370–380 cm^{-1} range. The bands at *ca* 370, 375, 372 and 360 cm^{-1} may be assigned to ν(Cr—O), ν(Mn—O), ν(Fe—O) and ν(Co—O) (metal–enolic oxygen) vibrations, respectively.[24,25] The ν(Co—O) band appears at a relatively lower region, consistent with six-coordinate geometry.

The far-IR spectra of chloro- and bromo-complexes of Cr^{III}, Mn^{III} and Fe^{III} exhibit bands at *ca* 340, 265; 335, 252; and 320, 245 cm^{-1} and are well within the ranges characteristic of ν(M—Cl) and ν(M—Br) vibrations, respectively. These values are intermediate between those reported for four- or six-coordinate complexes[26] and agree with those reported for five-coordinate complexes. The nitrato-complexes of all the metals show bands at *ca* 1260(ν_2), 1015(ν_3) and 805(ν_4) cm^{-1}, assignable to symmetric NO_2 stretching, NO stretching and non-planar deformation vibrations, respectively, and are consistent with the monodentate nature of the nitrato group.[26] The cobalt complex exhibits only a distinct medium band at *ca* 535 cm^{-1}, probably due to ν(Co—OH) vibrational modes, however, the new strong bands in the IR spectra of the cobalt(III) complex at *ca* 3500–3650 cm^{-1} may be assigned to ν(OH) of the coordinated hydroxyl group, which is further supported by the appearance of bands at *ca* 940 and 730 cm^{-1}, assignable to the twisting and wagging modes of water, respectively. The acetato-complex of manganese shows two bands at *ca* 1640 and 1390 cm^{-1}, which may be assigned to antisymmetric and symmetric (COO) stretching vibrations. These values indicate that the acetato group is coordinated and that the metal–oxygen bond thus formed is moderately covalent.[27] A broad band maximum is observed at *ca* 230 cm^{-1} in the spectrum of acetato complex and may be due to ν(Mn—OCO CH_3) vibrations.



$[M(Acac_2dap)X]_2$
X = Cl, Br, NO3 or NCS for M = Cr(III) or Fe(III)
X = Cl, Br, OAc or NCS for M = Mn(III)

The thiocyanato-complex of trivalent chromium, manganese and iron exhibits various bands at *ca* 2110(ν_1), 480(ν_2) and 830(ν_3), which may be assigned to ν(CN), NCS bending and ν(CS) of the NCS groups, respectively, characteristic of the N-bonded thiocyanate group.[28] This coordination mode is also supported by new bands at *ca* 270–280 cm^{-1}, assignable to (M—NCS).[9]

On steric grounds the complexes cannot be monomers[1,2] and in view of previous work in this field,[1,2,5–7] in conjunction with conductance, magnetic, electronic and IR spectral studies, we suggest that they may be binuclear.

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