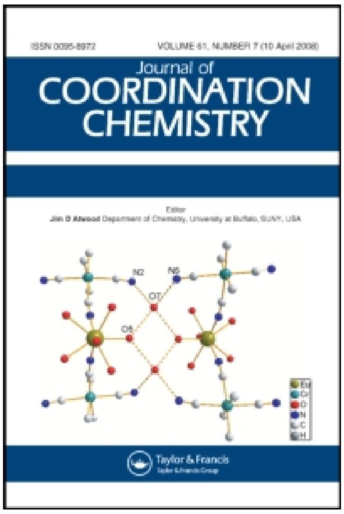

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BINUCLEAR DIVALENT METAL CHELATES BRIDGED BY AROMATIC DIAMINES

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Aromatic diamine Schiff bases derived from mono or dicarbonyl compounds are multidentate ligands which can act in a variety of ways. The oxygen or diamine groups may bridge two metal atoms and thus, may give rise to some unusual species.[1,2] This has led to the synthesis and characterisation of metal complexes with unusual structural and magnetic properties.[3,4] We report here, the isolation and characterisation of divalent manganese, iron, cobalt, nickel and copper complexes of bisacetylacetone-*m*-phenylenediamine ($Acac_2pola$) and bisacetylacetone-2,6-diaminopyridine ($Acac_2dap$).

EXPERIMENTAL

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

100 cm^3 methanolic solutions of 2,6-diaminopyridine or *m*-phenylenediamine (0.02 mol), acetylacetone (0.04 mol) and the divalent metal salts (0.02 mol) dissolved in methanol (50 cm^3) were mixed and refluxed for about 8 hours on a waterbath. The mixtures were concentrated to half volume and kept in a desiccator for about 3 days. The crystals which separated were filtered off, washed with acetone, then ether and dried under vacuum. Yield ~ 65%. All the complexes are stable up to about 300°. They are partially soluble in methanol, DMF, DMSO but insoluble in other common organic solvents. Those of copper are soluble in nitrobenzene. The physical and analytical measurements were made as reported earlier.[8]

RESULTS AND DISCUSSION

The analytical data given in Table I reveal a 1:1 metal to ligand stoichiometry for all the complexes. Molecular weight measurement made on the copper complexes show their dimeric nature.

The i.r. spectra of the free ligands show a broad stretching band at about 3200 cm^{-1} due to OH or NH groups which disappears in the spectra of the complexes. There is no free carbonyl absorption. It is also clear that the six-membered rings containing the hydrogen bonds are greatly stabilised by conjugation as is the case with β-diketones and salicylaldehyde. The other strong absorption bands between 1590 and 1580 cm^{-1} in the ligands accompanied by weaker absorptions between 1550 and 1560 cm^{-1} are assigned to C = C stretching vibrations. The bands at 1590 – 1580 cm^{-1} are shifted to slightly higher frequencies upon chelation, while those at 1550-1560 cm^{-1} shift to a lesser extent. The bands found at 1450-1460 cm^{-1} in the free ligands assigned to NH deformations, are not observed in the spectra of the chelates. Another band at about 1150 cm^{-1} is assigned to C–O stretching and is shifted to lower wave numbers by

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TABLE I
Analytical Data for the Complexes.

Complex	Colour	Found (%)				Calculated (%)			
		M	C	H	N	M	C	H	N
$[Mn(C_{16}H_{18}N_2O_2)]$	Black	16.62	58.18	5.46	8.34	16.92	59.07	5.53	8.61
$[Fe(C_{16}H_{18}N_2O_2)]$	Dark Brown	16.88	59.00	5.48	8.16	17.17	58.89	5.52	8.58
$[Co(C_{16}H_{18}N_2O_2)]$	Brown	17.89	58.15	5.32	8.40	17.93	58.35	5.47	8.51
$[Ni(C_{16}H_{18}N_2O_2)]$	Green	17.35	58.86	5.89	8.17	17.68	58.53	5.78	8.33
$[Cu(C_{16}H_{18}N_2O_2)]$	Brownish Black	18.94	56.90	5.46	8.19	19.04	57.57	5.39	8.39
$[Mn(C_{15}H_{17}N_3O_2)]$	Dark brown	16.24	54.82	5.11	12.63	16.47	55.21	5.21	12.88
$[Fe(C_{15}H_{17}N_3O_2)]$	Dark brown	17.22	55.19	5.29	12.68	17.12	55.04	5.19	12.84
$[Co(C_{15}H_{17}N_3O_2)]$	Light brown	17.28	53.90	5.27	12.01	17.87	54.54	5.15	12.52
$[Ni(C_{15}H_{17}N_3O_2)]$	Brown	16.98	54.02	5.21	12.21	17.32	54.71	5.16	12.46
$[Cu(C_{15}H_{17}N_3O_2)]$	Brownish red	18.61	53.26	5.00	12.01	18.98	53.81	5.08	12.35

chelation.[6] The spectrum of Acac$_2$dap shows various vibrational modes of the pyridine ring (1570-1580, 1460-1490, and 1430-1445 cm^{-1}). These do not change much in position or intensity on complexation and this rules out the possibility of pyridine coordination.[7,8] The other vibrations of the pyridine ring observed have similar behaviour and support this conclusion.[7-9]

The magnetic moments are well within the range reported for four-coordinate complexes.[10] The magnetic susceptibility of the Acac$_2$pda complexes were measured down to 85K and it has been observed that the μ_{eff} value per metal ion varies from 5.94 – 5.58 (Mn complex), 5.18 – 4.60 (Fe complex), 4.42 – 3.79 (Co complex) and 3.44 – 2.60 B.M. (Ni complex). The decrease in μ_B with temperature may indicate the presence of antiferromagnetic interactions in these complexes.[11] The Curie-Weiss law is obeyed with θ values of $-18°$ (Mn complex), $-30°$ (Fe complex) and $-48°$ (Co complex). The values of θ also indicate the presence of antiferromagnetic interactions.[12] Thus, it seems that the phenylenediamine or diaminopyridine groups are acting as bridges in the complexes. No such structures however have been reported but complexes formed by *m*-phenylenediamine and salicylaldehyde have been found to show similar effects.[3]

The electronic spectra of all the complexes recorded in DMF solution exhibit band absorption bands consistent with the distorted tetrahedral geometry of these complexes,[13] (Table II). The true structures lie between tetrahedral and square-planar arrangements and such distortion is indicated by the electronic spectra. The values of Dq, B and β calculated are in accordance with such a conclusion.

The far i.r. spectra of the ligands have not been previously reported. The bands at 610 and 410 cm^{-1} in the spectra of ligand Acac$_2$dap, assigned to the 6a and 16b vibrational modes of pyridine ring respectively,[14] do not show any changes on chelation thus confirming the results arrived at by conventional i.r. spectra.[15]

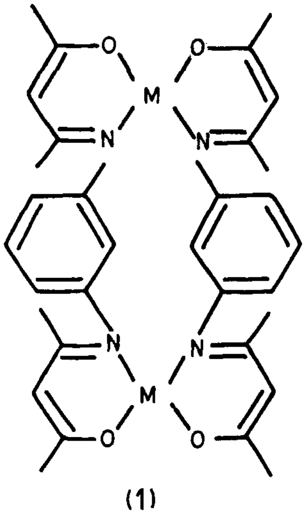
The new bands observed between 380 and 520 cm^{-1} in all the complexes have their origin in metal-nitrogen and metal-oxygen stretching modes. The bands at 460-470, 480-490, 485-510, 480-515 and 450-455 cm^{-1} may be assigned to ν(Mn-N), ν(Fe-N), ν(Co-N), ν(Ni-N) and ν(Cu-N) (azomethine) vibrations, respectively.[16,17] Two frequencies

TABLE II
Magnetic and Electronic Spectral Data.

Complex	Spectral maxima ($\mathrm{cm^{-1}}$)	10 Dq ($\mathrm{cm^{-1}}$)	Reach Parameters ($\mathrm{cm^{-1}}$)		Nephelauxetic Ratio β	μ_{eff} (B.M.)
			B	C		
$[\mathrm{MnAcac_2pda}]_2$	22450, 25350, 19400	6260	634	3220	0.66	5.94
$[\mathrm{Fe(Acac_2pda}]_2$	5650	5650				5.18
$[\mathrm{CoAcac_2pda}]_2$	6750, 14700	3170	796	3184	0.71	4.42
$[\mathrm{NiAcac_2pda}]_2$	7850, 11850	4223	588	2352	0.54	3.44
$[\mathrm{CuAcac_2pda}]_2$	13500, 15200, 18600					1.90
$[\mathrm{MnAcac_2dap}]_2$	23950, 25400, 19950	7824	483	3824	0.50	5.98
$[\mathrm{FeAcac_2dap}]_2$	5800	5800				5.12
$[\mathrm{CoAcac_2dap}]_2$	6500, 15200	3473	752	3008	0.67	4.48
$[\mathrm{NiAcac_2dap}]_2$	7900, 15620	4280	844		0.78	3.46
$[\mathrm{CuAcac_2dap}]_2$	13550, 15150, 18550					1.92

assignable to ν(M-O) vibrations have been observed at 220-420 $\mathrm{cm^{-1}}$ for 1:2 and 1:3 metal-acac complexes.[18] The bands observed at 290 and 395, 295 and 415, 300 and 410, 295 and 425, and 305 and 440 $\mathrm{cm^{-1}}$ may thus be assigned to the ν(M-O) vibrations[19] of the Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) complexes, respectively. These bands are in higher ranges than those suggested for five- or six-coordinate complexes and this again points towards the four-coordinate environment of the metal atoms.

The X-ray powder patterns of representative members of the divalent metal complexes are almost identical and thus, indicate that they are isomorphous. Based on the analytical, conductance, magnetic, electronic and i.r. spectral results, the structures shown below are proposed for these complexes.



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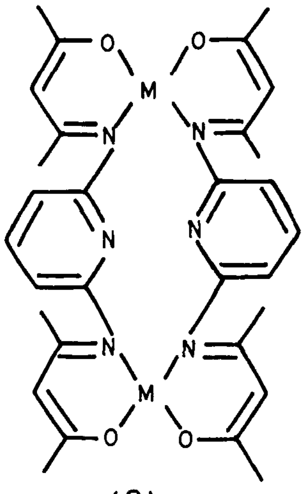

(2)

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