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SYNTHESIS AND CHARACTERIZATION OF SOME BINUCLEAR TRANSITION METAL COMPLEXES OF A BINUCLEATING LIGAND

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Abstract—Five binuclear transition metal(II) complexes, $[Mn_2L(\mu\text{-}Cl)Cl_2]$, $[Fe_2L(\mu\text{-}Cl)Cl_2]$, $[Co_2L(\mu\text{-}Cl)Cl_2]$, $[Ni_2L(\mu\text{-}Cl)Cl_2(H_2O)_2](H_2O)_2$ and $[Zn_2L(\mu\text{-}Cl)Cl_2]$, were synthesized, where HL is the binucleating ligand 2,6-diformyl-4-methylphenoldi(benzoylhydrazone). Based on the IR spectra, elemental analyses, conductivity measurements and thermal analysis, these complexes are proposed to have an endogenous phenoxide bridge and an exogenous chloride bridge. The ligand field parameters of the nickel(II) complex were obtained from near-IR spectra. The variable magnetic susceptibility (4–300 K) data of the manganese(II), iron(II), cobalt(II) and nickel(II) complexes indicated that the magnetic interactions between metal ions were very weak.

There is a growing interest in μ-phenolato bridged binuclear transition metal complexes derived from binucleating ligands, which arises from the areas of homogeneous catalysis, magnetic exchange between paramagnetic centres and bioinorganic chemistry.[1–3] In 1979, Lambert and Hendrickson[4] reported the preparation and characterization of a series of transition metal complexes with the general composition LM_2X_2 where H_2L is the macrocyclic binucleating ligand derived from 2,6-diformyl-4-methylphenol and 1,3-diaminopropane, M is divalent manganese, iron, cobalt, nickel, copper or zinc, and X is a coordinated anion. In this case, the metal ions were bridged by the same phenoxide group and the coordination geometry was essentially square pyramidal. We have synthesized and characterized the unsymmetrical bridged binuclear copper(II) complex using the 2,6-diformyl-4-methylphenol as backbone.[5] The complex had the composition $[Cu_2L(\mu\text{-}Cl)Cl_2]$, where HL is derived from 2,6-diformyl-4-methylphenol and benzoyl hydrazide (see structure). In this paper, we have expanded our research on transition metal(II) complexes other than that of copper(II).

HL
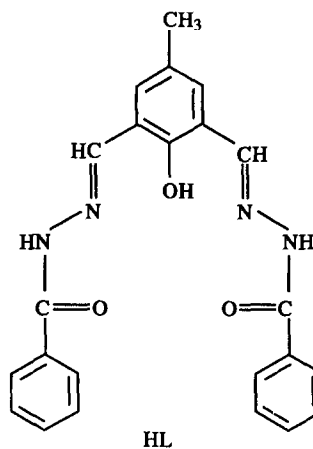
EXPERIMENTAL

Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out on a Perkin–Elmer elemental analyser model 240. IR spectra were recorded as compressed

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KBr pellets using an IR-408 spectrometer. Molar conductances were obtained on a DDS-11A conductometer. Thermal analyses were carried out with a Du Pont derivatograph model 1090B. The UV–vis spectra in dimethylformamide solution were recorded on a Shimadzu 240 UV spectrophotometer. The near-IR spectra in dimethylformamide solution were recorded on a Shimadzu 365 UV-NIR spectrophotometer. The magnetic susceptibilities of the complexes were measured over the 4.2–300 K temperature region with a vibrating-sample magnetometer model CF-1. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms, and the magnetic moments were calculated by the equation $\mu_{\text{eff}} = 2.828(\chi T)^{1/2}$.

Preparation of complexes

The manganese(II), iron(II), cobalt(II), nickel(II) and zinc(II) complexes were obtained by a similar procedure to that used for the copper(II) complex reported previously.[5] Since the manganese(II), iron(II) and cobalt(II) complexes may be oxygen sensitive in solution, these complexes were synthesized under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Composition and coordination geometry

The analytical data listed in Table 1 indicate that the complexes formed were binuclear. The molar conductance values (see Table 1) in dimethylformamide (DMF) fall in the expected range of non-electrolytes, indicating that the chloride ions are inside the coordination sphere and the complexes have the formula $[M_2L(\mu\text{-Cl})Cl_2]$. Thermal analysis for the nickel complex shows two significant weight losses corresponding to the elimination of four water molecules per binuclear unit in the temperature ranges 80–110°C and 224–230°C, respectively. Therefore, two water molecules are coordinated to the metal ions and occupy another

axis site, the other two water molecules are outside the coordination sphere and the nickel ions are in a distorted octahedron environment. This is in agreement with nickel's propensity to form stable, six-coordinate species.[6] The coordination geometry of the complexes other than the nickel complex is essentially square pyramidal[6,7] and is shown in Fig. 1.

IR spectra

The free ligand HL shows two sharp IR bands at 1650 and 1540 cm^{-1} attributable to the $v(C{=}O)$ and $v(C{=}N)$ stretching vibrations. The $v(C{=}O)$ bands shift to 1595–1630 cm^{-1} and $v(C{=}N)$ bands shift to 1550–1565 cm^{-1}, respectively, on formation of complexes. The $v(NH)$ absorption of hydrazone of the free ligand at 3070 cm^{-1} is observed at 3090–3180 cm^{-1} for the five complexes. The nickel complex shows a broad band at ca 3400 cm^{-1} which should be assigned to $v(H_2O)$ absorption.

UV–Vis near-IR spectra

The distinguishable absorption bands of UV–vis spectra of the complexes in DMF solution are listed in Table 2. The strong absorption peaks between 260 and 360 nm can be assigned to π–π^* transition of the ligand. The medium absorption peaks at ca 415 nm are the charge-transfer transition from the
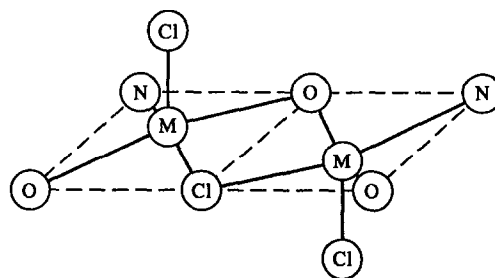

Fig. 1. Coordination environment of metal(II) ions.

Table 1. Analytical results and molar conductances for the complexes

Empirical formula of complex	Colour of solid complex	Found (%)			Calc. (%)			Λm $(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$
		C	H	N	C	H	N	
$[Mn_2L(\mu\text{-Cl})Cl_2]$	yellow	45.3	3.5	9.3	44.8	3.1	9.1	30
$[Fe_2L(\mu\text{-Cl})Cl_2]$	dark	44.6	2.7	8.9	44.7	3.1	9.1	21
$[Co_2L(\mu\text{-Cl})Cl_2]$	green	44.4	3.1	8.6	44.3	3.0	9.0	40
$[Ni_2L(\mu\text{-Cl})Cl_2]\cdot 4H_2O$	yellow	40.1	3.7	8.0	39.7	3.9	8.0	10
$[Zn_2L(\mu\text{-Cl})Cl_2]$	yellow	43.5	3.3	8.7	43.4	3.0	8.8	32

Table 2. The UV–vis and IR absorption spectra for the complexes

Complex	UV–vis (nm)		IR (cm^{-1})		
	Charge-transfer	d–d	C=O	C=N	—NH
$[Mn_2L(\mu\text{-}Cl)Cl_2]$	267, 325, 415		1615	1550	3150
$[Fe_2L(\mu\text{-}Cl)Cl_2]$	264, 302	600	1615	1555	3180
$[Co_2L(\mu\text{-}Cl)Cl_2]$	265, 315, 416	608, 675	1625	1560	3150
$[Ni_2L(\mu\text{-}Cl)Cl_2] \cdot 4H_2O$	268, 332 (sh), 345, 360 (sh), 416, 435 (sh)	598, 755	1630	1555	3140
$[Cu_2L(\mu\text{-}Cl)Cl_2]$	265, 342, 402, 421 (sh)	694	1620	1545	3100
$[Zn_2L(\mu\text{-}Cl)Cl_2]$	260, 316		1615	1550	3150

phenoxide of the ligand to metal ions (LMCT). The d–d transition can be observed in the visible region only for the iron, cobalt, nickel and copper complexes.

The near-IR spectra of iron and nickel complexes were determined in DMF solution. As an example, the near-IR spectrum as well as UV–vis spectrum of the nickel complex is shown in Fig. 2. The spectrum of nickel(II) d^8 generally has three spin-allowed transitions in O_h symmetry. The assignments of those bands are as follows :

$$^3T_{2g} \leftarrow \, ^3A_{2g} \, (\nu_1), \quad ^3T_{1g} \leftarrow \, ^3A_{2g} \, (\nu_2),$$

$$^3T_{2g}(P) \leftarrow \, ^3A_{2g} \, (\nu_3).$$

The shoulder peak of LMCT ($22{,}988 \, cm^{-1}$) can be assigned to ν_3 because ν_3 is almost observed in the UV range.[8] The strongest absorption in the near-IR range ($9091 \, cm^{-1}$) is assigned to ν_1. Values of ν_2, D_q and B were obtained from Lever's transition energy ratio :[9] $\nu_2 = 13{,}327 \, cm^{-1}$, $D_q = 909.1 \, cm^{-1}$ and $B = 602.8 \, cm^{-1}$. ν_2 is in good agreement with the experimental data ($13{,}255 \, cm^{-1}$). The calculated value of $\beta = B_{complex}/B_{free \, ion} = 0.585$ shows strong covalent bonding of nickel in the complex.

There is strong absorption at $5208 \, cm^{-1}$ and a relatively weak absorption at $9180 \, cm^{-1}$ for the iron complex. The two apparent absorption peaks can be assigned to the $^5A_1 \leftarrow \, ^5T_2$ and $^5B_1 \leftarrow \, ^5T_2$ transitions of iron(II) in a square pyramidal environment.[10]

Magnetic properties

The variable temperature susceptibilities of complexes of manganese, iron, cobalt and nickel were recorded in the 4.2–300 K region. The magnetic susceptibilities of all the complexes increase continuously upon cooling and the effective magnetic moments are constant in the range of 50 K to room temperature. This indicates that weak antiferromagnetic exchange interactions are present in these complexes.

The expression for the magnetic susceptibility derived from the spin Hamiltonian ($H = -JS_1 \cdot S_2$, $S_1 = S_2$) has been reported[11] and will not be reproduced here. The magnetic susceptibility and effective magnetic moment data were fitted to these
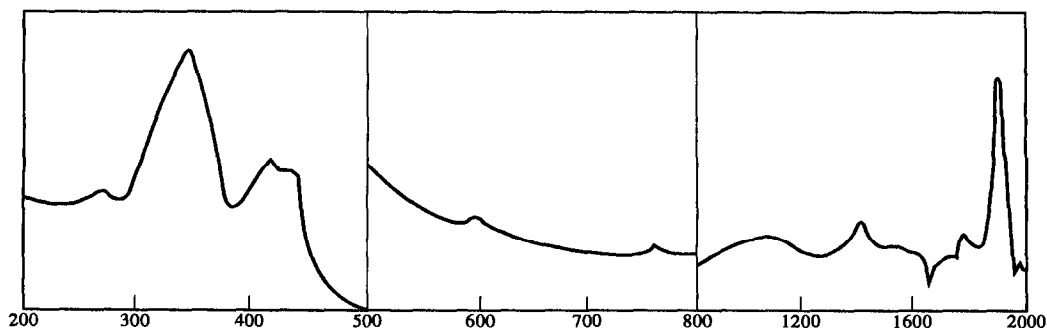

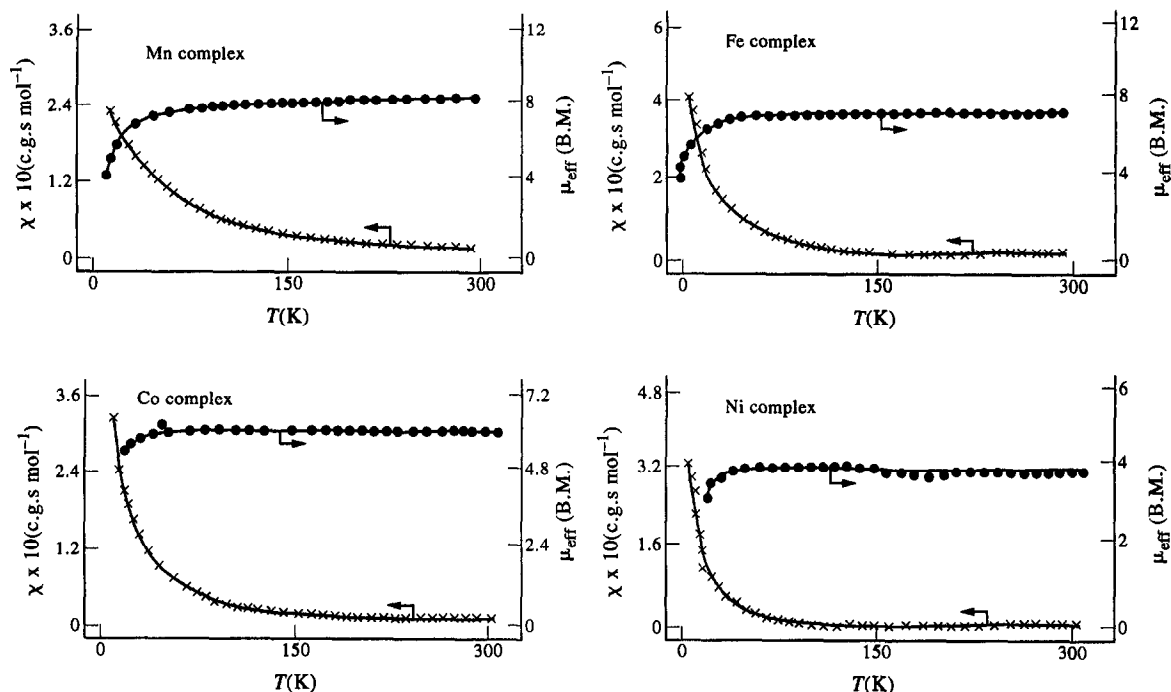Fig. 2. The UV–vis near-IR spectrum of the nickel(II) complex.

Fig. 3. Magnetic susceptibility and effective moment plotted as a function of temperature for manganese(II), iron(II), cobalt(II) and nickel(II) complexes. The curves through the data points are the best fits as described in the text using the parameters listed in Table 3.

equations and are illustrated in Fig. 3. The best parameters of fit are listed in Table 3.

The analysis of the magnetic results shows that the antiferromagnetic exchange interaction of manganese, iron, cobalt and nickel complexes is very weak and significantly less than in the copper(II) complex. This is in keeping with the magnitude of change that was observed by Glick and Lintvedt[12] and Lambert and Hendrickson.[4] A smaller antiferromagnetic coupling of the chloride-bridged complexes has been observed in comparison with that of phenoxide-bridged complexes of the LM_2X_2 series. As shown by Cairns and Busch[13] and Mallah et al.,[14] theoretical analysis from the viewpoint of electronegativity predicts a more efficient overlap integral for the phenoxide when the phenoxide and chloride are in equivalent bridging configurations.

Table 3. The magnetic susceptibility parameters for the complexes

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
S	5/2	2	3/2	1	1/2
Ionic radius (Å)	0.82	0.78	0.74	0.70	0.65
J (cm^{-1})	-1.35	-0.81	-0.84	-0.94	-76.4
g	2.02	2.13	2.22	2.02	2.18
$R^a \times 10^{-3}$	0.5	0.1	6.9	2.1	3.5

$^a R = \Sigma(\chi_{obs} - \chi_{calc})^2 / \chi_{obs}^2$.

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