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DINUCLEAR CU^{II} AND NI^{II} COMPLEXES OF 2:6–DIFORMYL *P*–CRESOL DIOXIME CIS TRANS TOPOLOGY AND EXTENSION OF A *CIS*–CU^{II}₂ COMPLEX TO A PENTANUCLEAR CU^{II}CU^{II}MN^{II}CU^{II}CU^{II} COMPLEX

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ABSTRACT: 2:6–Diformyl–p–cresol Dioxime (H₃L) formed the dinuclear Cu^{II} and Ni^{II} complexes $[Cu_2(C_9H_8N_2O_3)_2]0.5H_2O$ (1) Na $[Cu_2(C_9H_8N_2O_3)$ (C₉H₇N₂O₃)].3H₂O (2) and Ni₂(C₉H₈N₂O₃)₂]2.5H₂O (3). The structure of Na[Cu₂(C₉H₈N₂O₃) (C₉H₇N₂O₃)(H₂O)] (2ⁱ) and [Ni₂(C₉H₈N₂O₃)₂(H₂O)₄]8H₂O have been determined by X-ray crystallography. Complex Na[Cu₂(C₉H₈N₂O₃) (C₉H₇N₂O₃)]₃H₂O (2) has a cis arrangement of the two ligands providing dissimilar [CuN₂O₂] and [CuO₄] chromophores sharing the two phenolic oxygen atoms. The N₂O₂ cavity has a hydrogen bonded N–O---H---O–N linkage as the lateral chain and the Cu-in this site has a square pyramidal geometry with a water molecule at the axial site. The Cu in the O₄ cavity has a planar geometry. Complex $[Ni_2(C_9H_8N_2O_3)_2]2.5H_2O$ (3) has a trans configuration with respect to its two ligands and each Ni has a six coordinate geometry with two water molecules at the axial sites. Complex $[Cu_2(C_9H_8N_2O_3)_2] 0.5H_2O(1)$ has a trans configuration based on its having a chemical formula and IR-spectrum similar to $[Ni_2(C_9H_8N_2O_3)_2]$ 2.5H₂O (3). The following inter conversion among dinuclear Cu- complexes has been established by pH-adjustment: trans \implies Cis-(1) $[Cu_2(C_9H_8N_2O_3)(C_9H_7N_2O_3)]$ $[Cu_2(C_9H_8N_2O_3)_2]$ (2)trans $[Cu_2(C_9H_7N_2O_3)_2]^{2-}$ (water molecules are omitted). On the other hand $[Ni_2(C_9H_8N_2O_3)_2]^{2-}$ (3) showed the following inter conversion trans– $[Ni_2(C_9H_8N_2O_3)_2](3) \equiv trans- [Ni_2(C_9H_7N_2O_3)_2]^{2-}$. The cis complex $Na-[Cu_2(C_9H_8N_2O_3)(C_9H_7N_2O_3)]3H_2O$ (2) was reacted with Mn^{II} to afford $[Mn{Cu_2(C_9H_8N_2O_3)(C_9H_7N_2O_3)}_2(H_2O)_4]H_2O.$ 2DMF (4) that has a linear pentanuclear Cu^{II} Cu^{II} Mn^{II} Cu^{II} Cu^{II} structure formed by the coordination of two molecules of Na[Cu₂(C₉H₈N₂O₃)(C₉H₇N₂O₃)₂]3H₂O (2) to a Mn^{II} through oximino group.

INTRODUCTION

Metal-condensed compounds are currently the subject of many studies because of interest in their physicochemical properties and functions arising from the interaction or interplay of metal ions in close proximity. In order to provide metal-condensed compounds, 'complex ligands' having one or more sites capable of donating to another metal ion(s) are often used. Complex ligands with cis dioximate groups within the molecular framework are of particular interest¹⁻⁹ because the dioximate bridge is known as a good magnetic mediator between a pair of metal ions. For example, complete spin-coupling occurs at Cu^{II} room temperature in dioximate-bridged trinuclear complexes derived from bis(dimethylglyoximato)cuprate(II). Recent focus is placed on dinuclear and trinuclear complexes with cis dioximate groups as building blocks for providing metal-condensed systems. Typical examples are the extension of a dinuclear $Ni^{II}Ni^{II}$ complex to a tetranuclear Fe^{III} Ni^{II} Ni^{II} Fe^{III} system 7 extension of heterodinuclear $M_b^{II} M_c^{II}$ complexes to a trimettalic MaIII ($M_b^{II} M_c^{II}$) system and extension of a trinuclear $Cu^{II} Mn^{II} Cu^{II}$ complex to a polymeric [($Cu^{II} Mn^{II} Cu^{II}$) Mn^{II}]_n system⁹ through cis– dioximate bridges. In the polymeric compound a long-range magnetic ordering of $T_c = 5.5$ K has been confirmed.

In this context it is important to search simple dinuclear building blocks having a cis dioximate bridging group. 3–Formylsalicylic acid itself and Schiff bases with primary amines are known to afford dinuclear complexes of the $M_2(L)_2$ type with a trans arrangement of two ligands.^{10,11} Analogous 2:6–Diformyl p–cresol oxime (Chart 1, abbreviated as H₃L) is expected to show cis/trans topology in M_2L_2 type complexation, depending upon the absence or presence of an interaction between two oxime groups within a dinuclear molecule. In this work the following dinuclear Cu^{II} and Ni^{II} complexes have

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been derived from H₃L: $[Cu_2(HL)_2]$. 0.5H₂O (1), Na[Cu₂(HL)(L)].3H₂O (2) and $[Ni_2(HL)_2]$.2.5H₂O (3). The cis arrangement of the two ligands in 2 and the trans arrangements in 3 have been proved by X-ray crystallography, and the following interconversion by pH has been established for the complexes; trans- $[Cu_2(HL)_2](1) \implies$ cis- $[Cu_2(HL)(L)]^-$ (2) \implies trans- $[Cu_2(L)_2]_2^-$ and trans- $[Ni_2(HL)_2]$ (3) \implies trans- $[Ni_2(L)_2]_2^{2-}$ (water molecules are omitted). The reaction of 2 with Mn^{II} ions has afforded [Mn{Cu₂(HL)(L)}₂] (4) whose structure is studied along with its magnetic properties.



EXPERIMENTAL

Physical Measurements

Elemental analyses of carbon, hydrogen and nitrogen were obtained at The Analytical Division C.D.R.I., Lucknow. Metal analyses were made on a Shimadzu AA-680 Atomic Absorption/Flame Emission Spectro-photometer. Infrared spectra were measured using KBr disks with a Perkin–Elmer Specturm BX FT–IR system. Electronic absorption and reflectance spectra were recorded on a Shimadzu UV–3100PC Spectrophotometer. Magnetic susceptibilities of powdered samples were measured on a Quantum Design MPMS XL SQUID susceptometer in the temperature range 2–300 K. Diamagnetic corrections were made using Pascal's constants.¹²

PREPARATIONS OF ORGANIC COMPOUND AND ISOLATION OF COMPLEXES

(A) **Bis(3–Hydroxy imino methyl)4–methyl phenol (H**₃**L).** A mixture of an ethanol solution (150 cm³) of 2:6–diformyl–4–methyl phenol¹³ (1.66 g, 10 mmol) and an aqueous solution (50 cm³) of hydroxylamine hydrochloride (1.04 g, 15 mmol) were mixed and together with an aqueous solution (10 cm³) of NaOH (0.60 g, 15 mmol) were refluxed for 5 hours and then evaporated to dryness. The residue was stirred with an aqueous NaHCO₃ solution (5%, 100 cm³), and the aqueous extract separated from any insoluble material was neutralized with dilute hydrochloric acid to give a colorless precipitate. This was filtered off, thoroughly washed with water and dried in vacuo. The yield was 1.31 g (72%). Anal. Found: C, 55.50, H, 5.0, N, 14.40. Calcd for (C₉H₁₀N₂O₃) : C, 55.67, H, 5.15, N, 14.43% IR [v/cm⁻¹] as KBr disk: 3217, 1660, 1611, 1450, 1317, 1249, 1228, 1189, 957, 761, 681.

1. $[Cu_2(HL)_2].0.5H_2O$ (1). A solution of H₃L (18 mg. 0.1 mmol) in dimethylformamide (DMF) (3 cm³) was layered with a solution of copper(II) perchlorate hexahydrate (37 mg, 0.1 mmol) in water (2 cm³) and allowed to stand at ambient temperature. After several days the resulting green microcrystals were separated, washed with diethyl ether and dried in vacuo. The yield was 21 mg (85%). Anal. Found: C, 40.80, H, 3.10, N, 10.49, Cu, 23.88. Calcd. for (C₁₈Cu₂H₁₇N₄O₇). C, 36.79, H, 3.57, N, 9.53, Cu, 21.64%. IR[v/cm⁻¹] as KBr disk: 3367, 1600, 1573, 1432, 1360, 1267, 1230, 981, 883, 766, 626. UV-vis [λ /nm(ϵ /M⁻¹cm⁻¹)]: 657 [powder]; 628 (315) [in 0.1M NaOH solution].

2. **Na**[**Cu**₂(**HL**)(**L**)].**3H**₂**O** (2). H₃L (181 mg, 1.0 mmol) was dissolved in an aqueous solution (100 cm³) of NaOH (120 mg, 3.0 mmol). To this was added an aqueous solution of copper(II) acetate monohydrate (200 mg, 1 mmol), and the mixture was heated at reflux for one hour. The resulting green crystals were separated and recrystallized from an aqueous NaOH solution (0.4%, 100 cm³). The yield was 160 mg (57%). Anal. Found: C, 36.62, H, 3.40, N, 9.39, Cu, 21.50 Calcd. for (C₁₈Cu₂H₂₁N₄NaO₉). C, 36.79, H, 3.57, N, 9.53, Cu, 21.64%. IR[v/cm⁻¹] as KBr disk: 3488, 3076, 2998, 2923, 2853, 1607, 1586, 1430, 1348, 1269, 992, 754. UV-vis [λ /nm(ϵ /M⁻¹cm⁻¹)]: 566 and 664 [powder]; 627 (320) [in 0.1M NaOH solution].

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3. [Ni₂(HL).2.5H₂O (3). H₃L (181 mg, 1.0 mmol) was dissolved in an aqueous solution (100 cm³) of NaOH (80 mg, 2.0 mmol). To this was added an aqueous solution (50 cm³) of nickel(II) acetate tetrahydrate (248 mg, 1.0 mmol), and the mixture was allowed to stand for several days to afford [Ni₂(HL)₂(H₂O).8H₂O (3^b) as green crystals. Because they were highly efflorescent, elemental analyses were performed on the sample dried in air (3). The yield was 217 mg (83%). Anal. Found: C, 39.39, H, 3.71, N, 10.12, Ni, 10.61 Calcd. for Ni₂C₁₈H₂₁N₄O_{8.5}. C,39.53, H, 3.84, N, 10.24, Ni, 10.74%. IR[v/cm⁻¹] as KBr disk: 3447, 3369, 1595, 1568, 1449, 1341, 1267, 1228, 968, 882, 762, 679, 621. UV-vis [λ /nm(ϵ /M⁻¹cm⁻¹]: 617 and 1120 [powder]; 620 (43) and 1137(10) [in 0.1M NaOH aq. solution].

4. [Mn{Cu₂(HL)(L)}₂(H₂O)₄].H₂O.2DMF (4). To a solution of 2 Na[Cu₂(HL)(L)].3H₂O (52 mg, 0.1 mmol) in a DMF–H₂O mixture (1:1 in volume, 60 cm³) was added a solution of manganese(II) perchlorate hexahydrate (18 mg, 0.05 mmol) in DMF (10 cm³), and the mixture was allowed to stand at ambient temperature forming green needles after a few days. The crystals were obtained as [Mn{Cu₂(HL)(L)}₂(H₂O)₄]. H₂O.2DMF (4^b) based on X–ray crystallography as discussed later. In open air the compound loses three molecules of water to give [Mn{Cu₂(HL)(L)}₂(H₂O)]. H₂O.2DMF (4). The yield was 12 mg (19%). Anal. Found: C, 34.70, H, 4.20, N, 11.10, Cu, 20.40, Mn, 4.30 Calcd. for (C₃₆Cu₄₄H₅₄MnN₁₀O₁₉). C, 34.86, H, 4.35, N, 11.29, Cu, 20.51, Mn, 4.434%. IR[v/cm⁻¹] as KBr disk: 3369, 1655, 1603, 1548, 1433, 1234, 994, 765. UV-vis [λ /nm]: 650 [powder].

X-RAY CRYSTALLOGRAPHY

A single crystal of Na[Cu₂(HL)(L)(H₂O)] (2^h) mounted on a glass fiber and a single crystal of [Ni₂(HL)₂(H₂O)₄].8H₂O (3^h) sealed in a glass tube were used for X-ray crystallographic measurements using a Rigaku AFC7R diffractometer with graphite monochromated Mo-K α radiation ($\lambda = 0.71069$ Å) and a 12 kW rotating anode generator. Cell constants and the orientation matrix for the data collection were obtained from 25 reflections and the ω -2 θ scan mode was used for the intensity collections at 23 ± 1°C. A single crystal of [Mn{Cu₂(HL)(L)}₂(H₂O)₄]. 4H₂O.2DMF (4^h) was mounted on a glass fiber and used for crystallographic measurements using a Rigaku RAXIS-RAPID imaging plate area detector. Intensity data were collected by taking oscillation photographs. Pertinent crystallographic parameters for 2^h, 3^h and 4^h are summarized in Table 6.1).

The structures were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure analysis but not refined. Computations were carried out on an IRIS O_2 computer using the TEXSAN crystallographic software package.¹⁴

	(4)		
	2	3	4
Empirical formula	$C_{18}Cu_2H_{17}N_4NaO_7$	$C_{18}H_{40}N_4Ni_2O_{18}$	$C_{36}Cu_4H_{60}MnN_{10}O_{22}$
Formula weight	551.08	717.56	1293.10
Crystal color	Green	Green	Green
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	P1 ⁻ (no. 2)	$P2_1/a$ (no. 14)	P1 ⁻ (no.2)
a/Å	9.347(3)	7.79(4)	11.2151(7)
b/Å	11.033(2)	15.561(4)	13.1298(7)
c/Å	8.607(2)	11.124(2)	8.2073(4)
a/°	101.65(2)	90.00	94.744(2)
β/°	92.07(2)	99.07(2)	99.760(2)
γ/°	75.28(2)	90.00	77.517(2)
$V/Å^3$	870.7(4)	1329.7(7)	1161.6(1)
Ζ	2	2	1

Table 6.1: Crystallographic parameters for Na[Cu₂(HL)L(H₂O)] (2^{\downarrow} [Ni₂(HL)₂(H₂O)₄].8H₂O (3^{\downarrow}) and [Mn{Cu₂(HL)(L)}₂(H₂O)₄].4H₂O.2DMF (4^{\downarrow})

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T/K	296	296	183	
$D_{calc}/g \ cm^{-3}$	2.075	1.728	1.878	
μ (Mo–K α)/cm ⁻¹	26.17	15.09	21.67	
No. observations (I >	3258	2379	3506	
3.00 σ(I))				
R ^a	0.034	0.033	0.033	
R _w	0.058^{b}	0.056 ^b	0.046 ^b	
G.O.F.	1.17	1.08	1.00	
		-1, 2, -2, -1/2		

 $R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|. {}^{b}R_{w} = [(\sum w(|F_{o}| - |F_{c}|)^{2} / \sum wF_{o}^{2})]^{1/2}.$ $R_{w} = [(\sum w(F_{o}^{2} - F_{c}^{2})^{2} / \sum w(F_{o}^{2})^{2})]^{1/2}, w = 1/[\sigma^{2}(F_{o})] = [\sigma^{2}c(F_{o}) + p^{2}F_{o}^{2}/4]^{-1}.$

Table 6.2: S	selected bond distances (Å) and angles (°) for $2^{ }$ ($(C_{18}H_{17}Cu_2N_4NaO_7)$

Cu(1)–O(2)	1.958(2)	Cu(2)–O(2)	1.900(2)
Cu(1)–O(6)	1.955(2)	Cu(2)–O(3)	1.883(2)
Cu(1)–N(1)	1.943(3)	Cu(2)–O(6)	1.916(2)
Cu(1)–N(2)	1.947(2)	Cu(2)–O(7)	1.889(2)
Cu(1)–O(9)	2.378(2)	Cu(1)Cu(2)	2.961(1)
O(2)–Cu(1)–O(6)	78.74(8)	O(2)–Cu(2)–O(3)	95.71(8)
O(2)-Cu(1)-N(1)	89.65(9)	O(2)–Cu(2)–O(6)	81.16(9)
O(6)–Cu(1)–N(2)	90.06(9)	O(3)–Cu(2)–O(7)	88.51(9)
N(1)-Cu(1)-N(2)	100.2(1)	O(6)–Cu(2)–O(7)	94.50(9)
Cu(1)–O(2)–Cu(2)	100.24(9)	Cu(1)–O(6)–Cu(2)	99.79(9)

RESULTS AND DISCUSSION

Crystal Structures

 $Na[Cu_2(HL)(L)(H_2O)](2^{l})$. An ORTEP¹⁵ view of 2^l is shown in Fig. 1 together with the atom numbering scheme. Relevant bond distances and angles are given in Table 6.2.

The results clearly demonstrate the cis arrangement of the two ligands (HL²⁻ and L³⁻) providing nonequivalent {CuN₂O₂} and {CuO₄} chromophores, sharing the two phenolic oxygen atoms. The Cu2...Cu1 interatomic separation is 2.961(1) Å. The N₂O₂ cavity has a hydrogen-bonded N1–O1...H...O5–N2 linkage formed by the dioximate group. The Cu1 in the N₂O₂ site has a square–pyramidal geometry with a water molecule at the apical site. The basal Cu–to–donor bond distances range from 1.943(3) to 1.958(2) Å. The axial Cu–O9 bond distance (2.378(2) Å) is elongated due to the Jahn–Teller effect of a d⁹ electronic configurations. The O1...O5 separation (2.444(3) Å) is very short relative to the O...O separation (2.53–2.70 Å) of bis(dimethylglyoximato) copper(II) [Cu(Hdmg)₂]¹⁶ and is similar to that (2.44 Å) of [Ni(Hdmg)₂].¹⁷ This fact indicates strong hydrogen bonding in the N1–O1...H9...O5–N2 linkage. The O1–H9 and H9–O5 separations are 1.385(2) and 1.210(2) Å, respectively. The Cu₂ in the O₄ site has a planar configuration with significantly short Cu₂–to–donor bond distances (1.883(2)–1.916(2) Å). The molecule except for the aqua ligand forms a good co–plane. The axial aqua molecule is hydrogen–bonded to the oximinato oxygen O8¹ of an adjacent molecule.

 $[Ni_2(HL)_2(H_2O)_4].8H_2O$ (3^b). An ORTEP drawing of 3^b is given in Fig. 2 together with the atom numbering scheme. Selected bond distances and angles are given in Table 6.3.

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Table 0.3. Selected bond distances (A) and angles ($)$ for 5 (C ₁₈₁₁₄₀₁ (1)(1)(2)(1)					
Ni(1)–O(2)	2.018(2)	Ni(1)–O(5)	2.075(2)		
Ni(1)-O(2*)	2.035(2)	Ni(1)–O(6)	2.130(2)		
Ni(1)–O(3)	2.005(2)	Ni(1) - N(1)	2.031(2)		
Ni(1)Ni(1*)	3.031(1)				
O(2)–Ni(1)–O(3)	88.82(7)	O(2) - Ni(1) - N(1)	86.65(9)		
O(2)-Ni(1)-O(5)	92.71(8)	O(3)–Ni(1)–O(5)	89.89(8)		
O(2)-Ni(1)-O(6)	90.82(8)	O(3)–Ni(1)–O(6)	88.41(8)		
O(2*)-Ni(1)-O(5)	90.38(8)	O(3)-Ni(1)-N(1*)	101.33(9)		
O(2*)-Ni(1)-O(6)	91.80(7)	O(5)-Ni(1)-N(1*)	90.43(9)		
O(2)-Ni(1)-O(2*)	83.19(7)	O(6)-Ni(1)-N(1*)	86.41(9)		
Ni(1)-O(2)-Ni(1*)	96.81(7)				

|--|

Symmetry operation: *-x, -y, -z.

The molecule has a dinuclear core with a trans arrangement of the two HL^{2-} ligands. There exists an inversion center at the center of the four–membered ring formed by the two Ni atoms and the two phenolic oxygen atoms. Four of the twelve water molecules are involved in axial donation to the Ni ions, providing a pseudo octahedral environment about each Ni. The in–plane Ni–to–donor bond distances range from 2.005(2) to 2.035(2) Å. The axial Ni–O bond distances are slightly longer (2.075(2) and 2.130(2) Å). The Ni…Ni* interatomic distance is 3.031(1) Å and the Ni–O2–NI* angle is 96.81(7)°. The two basal {NiNO₃} planes are coplanar but the two (HL)⁻ ligands are bent at the N1–O2–O3 edge with a dihedral angle of 32.94(8)°. Because of this bending, the bridging phenolic oxygen O₂ shows a non–planar configuration. That is, the sum of the angles C1–O2–Ni, C1–O2–Ni* and Ni–O2–Ni* (345.3°) is significantly smaller than 360°.

Six water molecules in the lattice are hydrogen-bonded to the complex molecule through the oxime hydrogen atom H4 (H4*) (O1...O2.705(4) Å), the oximinato oxygen atom O4 (O4*) (O4...O 2.819(3) Å), and the hydrogen attached to O6 (O6*) (O6...O: 2.819(3) Å). The remaining water molecules are captured in the crystal lattice.

It is interesting to compare the bite angles about the imine nitrogen N1* in compounds $2^{|}$ (C₁₈H₁₇Cu₂N₄NaO₇) and $3^{|}$ (C₁₈H₄₀N₄Ni₂O₁₈). The C7–N1–Cu1, C7–N1–O1 and Cu1–N1–O1 angles for $2^{|}$ (C₁₈H₁₇Cu₂N₄NaO₇) are 125.8, 116.0 and 118.2°, respectively, and the corresponding angles for $3^{|}$ (C₁₈H₄₀N₄Ni₂O₁₈) are 124.1, 111.4 and 123.5°, respectively. It is seen that the C7–N1–O1 angle in $2^{|}$ (C₁₈H₁₇Cu₂N₄NaO₇) is large relative to that in $3^{|}$ (C₁₈H₄₀N₄Ni₂O₁₈) whereas the Cu1–N1–O1 angle in $2^{|}$ (C₁₈H₁₇Cu₂N₄NaO₇) is small relative to that in $3^{|}$ (C₁₈H₄₀N₄Ni₂O₁₈). This fact adds support to the theory of strong hydrogen bonding in the N1–O1…H9…O5–N2 linkage in $2^{|}$ (C₁₈H₁₇Cu₂N₄NaO₇).

CIS/TRANS TOPOLOGY

The X-ray crystallographic studies have clearly demonstrated that 2 ($C_{18}H_{21}Cu_2N_4NaO_9$) has a cis configuration whereas 3($C_{18}H_{21}Ni_4N_4O_{8.5}$) has a trans configuration with respect to the arrangement of the two ligands. Complex 2($C_{18}H_{21}Cu_2N_4NaO_9$) shows a sharp IR band at 2853 cm⁻¹ that is attributable to the v(OH) mode of a coordinated aqua molecule. A hydrogen-bonded dioximate group (N-O...H...O-N) generally shows a v(OH) band at low frequency,¹⁸ however, 2 ($C_{18}H_{21}Cu_2N_4NaO_9$) shows no IR band attributable to an oxime group in the region 2000–1630 cm⁻¹. The oxime vibration can be located at lower frequency (< 1630 cm⁻¹) but is concealed by strong ligand IR bands. Complex 3($C_{18}H_{21}Ni_4N_4O_{8.5}$) shows two sharp IR bands at 3447 and 3369 cm⁻¹ superimposed on a broad band (3300–3500 cm⁻¹) due to lattice water. The former band can be assigned to the v(OH) mode of a coordinated water molecule and the latter band to the v(OH) mode of an oxime group. Complex 1 ($C_{18}H_{17}Cu_2N_4O_7$) certainly has a trans configuration judging from its chemical formula (HL²⁻: Cu = 2: 2) and IR spectrum showing the v(OH) band of an oxime group at 3367 cm⁻¹.

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Complexes 1 ($C_{18}H_{17}Cu_2N_4O_7$) and 3($C_{18}H_{21}Ni_4N_4O_{8.5}$) are insoluble in water and 2($C_{18}H_{21}Cu_2N_4NaO_9$) is sparingly soluble in water. The reflectance spectrum of 1 ($C_{18}H_{17}Cu_2N_4O_7$) exhibits one d–d band at 657 nm (Fig. 3), whereas that of 2($C_{18}H_{21}Cu_2N_4NaO_9$) has two d–d bands at 566 and 664 nm in accord with the non– equivalence about the two Cu^{II} ions. The reflectance spectrum of 3($C_{18}H_{21}Ni_4N_4O_{8.5}$) has two bands at 617 and 1120 nm that can be assigned to the ${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ and ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$ transitions, respectively, of the Ni^{II} under pseudo octahedral symmetry (Fig. 4).

Complex 1 ($C_{18}H_{17}Cu_2N_4O_7$) was converted into 2($C_{18}H_{21}Cu_2N_4NaO_9$) by treatment with an equimolar amount of NaOH in water, and 2 ($C_{18}H_{21}Cu_2N_4NaO_9$) was converted into 1($C_{18}H_{17}Cu_2N_4O_7$) by treatment with acid. Both 1($C_{18}H_{17}Cu_2N_4O_7$) and 2($C_{18}H_{21}Cu_2N_4NaO_9$) are soluble in aqueous NaOH solution (excess NaOH) and show the same absorption spectrum with one visible band at ca. 627 nm (ε 320 M⁻¹ cm⁻¹) (See insert of Fig.3). The species existing in alkaline solution must be [$Cu_2(L)_2$]²⁻ containing the fully–deprotonated ligand L³⁻, and it may have a trans configuration as its visible spectrum is similar to the reflectance spectrum of 1($C_{18}H_{17}Cu_2N_4O_7$). The acidification of the alkaline solution resulted in the precipitation of 1($C_{18}H_{17}Cu_2N_4O_7$). Thus, the following interconversion is established: trans–[$Cu_2(HL)_2$](1) $= cis-[Cu_2(HL)(L)]^-$ (2) $= trans-[Cu_2(L)_2]^{2-}$ (see Chart 2,a).

When 3 ($C_{18}H_{21}Ni_4N_4O_{8.5}$) was treated with an equimolar amount of NaOH in water about one half of the sample dissolved and the resulting yellowish green solution showed two absorption bands at 620 and 1137 nm. Complex 3($C_{18}H_{21}Ni_4N_4O_{8.5}$) was completely dissolved in an aqueous solution containing excess NaOH to give the same absorption spectrum as observed above (see insert of Fig. 4). The species existing in the alkaline solution must be trans $-[Ni_2(L)_2(H_2O)_4]^{2-}$ judging from the marked spectral resemblance to 3($C_{18}H_{21}Ni_4N_4O_{8.5}$). The acidification of the alkaline solution resulted in the precipitation of 3. Thus, cis/trans topology is not the case of the dinuclear Ni complexes (Chart 2,b).

It is of value to consider why cis dinuclear Ni species corresponding to 2 cannot exist. The X-ray crystallography for $2^{|}$ (C₁₈H₁₇Cu₂N₄NaO₇) indicates that the [CuN₂O₂] chromophore has moderate Cu–N and Cu–O bond distances (1.943(3)–1.958(2)Å) whereas the {CuO₄} chromophore has short Cu–O bond distances (1.883(2)–1.916(2) Å). The N₂O₂ site may accommodate high–spin Ni^{II} by slightly enlarging the cavitiy, but the O₃ site is too small to accommodate high–spin Ni^{II}. It appears that the O₃ cavity is suitable for low–spin Ni^{II} with a short Ni–to–donor bond distance (< 1.9 Å), but Ni^{II} cannot be of low–spin in the O₃ site because the metal d_π orbitals are destabilized owing to the strong π –antibonding character of the phenolate and oximinato O atoms.¹⁹

PHYSIOCHEMICAL PROPERTIES

Complexes $1(C_{18}H_{17}Cu_2N_4O_7)$ and $2(C_{18}H_{21}Cu_2N_4NaO_9)$ each have a subnormal magnetic moment at room temperature (0.99 and 0.70 μ_B , respectively) suggesting an operation of antiferromagnetic interaction within the molecules. The χ_A vs. T curves for $1(C_{18}H_{17}Cu_2N_4O_7)$ and $2(C_{18}H_{21}Cu_2N_4NaO_9)$ are given in Fig. 5. The magnetic susceptibility for $1(C_{18}H_{17}Cu_2N_4O_7)$ decreased with decreasing temperature to a near plateau value of 50×10^{-6} cm³ mol⁻¹ around 90 K and showed an increase below 50 K. The plateau value corresponds to the temperature–independent paramagnetism²⁰ arising from the second–order Zeeman effect. Similarly, the magnetic susceptibility of 2 $(C_{18}H_{21}Cu_2N_4NaO_9)$ continuously decreased with decreasing temperature to a plateau value of 60×10^{-6} cm³ mol⁻¹ near 110 K and showed an increase below 50 K. The slight increase in magnetic susceptibility at low temperature suggests the presence of paramagnetic impurities. Magnetic simultations were carried out using the Bleaney–Bowers equation²¹ involving a correction term for paramagnetic impurities (eqn. (1)):

$$\chi_{\rm A} = (1 - p) \{ N^2 g \beta^2 / kT \} [1 + \exp(-2J/kT)]^{-1} + p(Ng^2 \beta^2 / 4kT) + N\alpha (1)$$

where N is Avogadro's number, β is the Bohr magneton, k is the Boltzmann constant, J is the exchange integral, T is the absolute temperature, N α is the temperature–independent paramagnetism, and p is the fraction of paramagnetic impurity. A good magnetic simulation was obtained for $1(C_{18}H_{17}Cu_2N_4O_7)$ with eqn. (1), using magnetic parameters of g = 2.07, J = -255 cm⁻¹, N α = 50 × 10⁻⁶ cm³ mol⁻¹, and p=0.003.

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(2)

The discrepancy factor defined as $R(\chi) = [\sum (\chi_{obsd} - \chi_{calcd})^2 / \sum (\chi_{obsd})^2]^{1/2}$ was 0.053. Similarly, the cryomagnetic property of $2(C_{18}H_{21}Cu_2N_4NaO_9)$ was well reproduced by eqn. (1), using magnetic parameters of g = 2.07, J = -355 cm⁻¹, $N\alpha = 60 \times 10^{-6}$ cm³ mol⁻¹, and p = 0.0006. The discrepancy factor defined was 0.052.

The χ_A vs. T curve of $3(C_{18}H_{21}Ni_4N_4O_{8.5})$ is given in Fig. 6. The magnetic moment at room temperature is 3.07 μ_B which decreased with decreasing temperature to 0.46 μ_B at 2 K. The magnetic susceptibility increased with decreasing temperature to a maximum value at 28 K then decreased. Such cryomagnetic behavior is typical of a dinuclear Ni(*S*=1) Ni(*S*=1) system exhibiting an intramolecular antiferro-magnetic interaction. The increase in magnetic susceptibility at low temperature indicates the presence of a small amount of paramagnetic impurity. Thus, magnetic simulations for 3 were carried out using the magnetic susceptibility expression (2)²² including the correction term for the paramagnetic impurity:

 $\chi_{A} = (1 - p) \{ Ng^{2}\beta^{2}/kT \} [5 + \exp(-4J/kT)]/[5 + 3\exp(-4J/kT) + \exp(-6J/kT)] + p(2Ng^{2}\beta^{2}/3kT) + N\alpha$

The cryomagentic property of 3 (C₁₈H₂₁Ni₄N₄O_{8.5}) could be well reproduced by this equation using the magnetic parameters, $J = -10 \text{ cm}^{-1}$, g = 2.12, $N\alpha = 300 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ and p = 0.03. The discrepancy factor for the magnetic simulation was 0.056.

EXTENSION TO A PENTANUCLEAR SYSTEM

Complex $2(C_{18}H_{21}Cu_2N_4NaO_9)$ is of particular interest to us because it has a dioximate group capable of acting as a bridge to a second metal ion. In this study $2(C_{18}H_{21}Cu_2N_4NaO_9)$ was reacted with Mn^{II} in DMF to obtain [Mn{Cu₂(HL)(L)}₂ (H₂O)₄].H₂O.2DMF (4). An ORTEP view of [Mn{Cu₂(HL)(L)}₂(H₂O)₄]. H₂O.2DMF (4^h) is shown in Fig. 7 together with the atom numbering scheme. Selected bond distances and angles are given in Table 6.4.²³⁻²⁵

The X-ray crystallographic results demonstrate that a linear pentanuclear structure has been formed by the coordination of two $\{Cu_2(HL)(L)\}^-$ molecules to Mn^{II} through one outer oximinato oxygen. An inversion center exists at the Mn atom. Each $\{Cu_2(HL)(L)\}^-$ unit retains the geometric features found for $2^{l}(C_{18}H_{17}Cu_2N_4NaO_7)$ except that the axial donor on Cu1 is an aqua oxygen in but a carboxylate oxygen (O8^a) from an adjacent molecule in $4^{l}(C_{36}H_{60}Cu_4MnN_{10}O_{22})$ (Cu1–O8^a 2.403(3) Å). Furthermore, Cu₂ in the O₃ site in $4^{l}(C_{36}H_{60}Cu_4MnN_{10}O_{22})$ has a square–pyramidal geometry with the coordination of the oximate oxygen O5^b of an adjacent molecule (Cu2–O5^b 2.457(3) Å). The geometry about the Mn atom is pseudo octahedral with four water molecules on the equatorial base and two oxiiminoate oxygen atoms at the axial sites. The equatorial Mn–O9 and Mn–O10 bond distances are 2.193(3) and 2.155(3) Å, respectively. The axial Mn–O4 bond distance is significantly elongated (2.248(3) Å). The oximinoate O8^a bound to Cu1 and the oxime oxygen O5^b bound to Cu2 are situated trans to each other with respect to the mean molecular plane. As a result, $4^{l}(C_{36}H_{60}Cu_4MnN_{10}O_{22})$ has a two–dimensional network structure extended in the ac plane.



Chart 2 Structural changes of (a) dinuclear Cu complexes and (b) dinuclear Ni complexes

The four lattice water molecules are hydrogen–bonded to the complex molecule through the oxime oxygen atom O5 (O5^c) (O5...O 2.883(5) Å) and between the oximinoate oxygen atom O8 (O8^c) and the hydrogen attached to O10 (O10^c) (O8...O 2.803(4): O10...O: 2.715(4) Å). The two DMF molecules are also involved in hydrogen bonding to the hydrogen attached to O9 (O9^c) (O9...O(DMF): 2.657(4) Å). The two DMF molecules are also involved in hydrogen bonding to the hydrogen bonding to the hydrogen attached to O9(O9^c) (O9...O(DMF): 2.657(4)Å).

Cu(1)–O(2)	1.960(3)	Cu(2)–O(2)	1.923(3)
Cu(1)–O(6)	1.948(3)	Cu(2)–O(3)	1.875(3)
Cu(1)–O(8 ^a)	2.403(3)	$Cu(2) - O(5^{b})$	2.457(3)
Cu(1)–N(1)	1.936(3)	Cu(2)–O(6)	1.914(3)
Cu(1)–N(2)	1.946(3)	Cu(2)–O(7)	1.897(3)
Mn–O(4)	2.248(3)	Mn–O(9)	2.193(3)
Mn-O(10)	2.155(3)	Cu(1)Cu(2)	2.99(1)
Cu(2)Mn	5.025(1)	Cu(1)Mn	7.729(1)
O(2)–Cu(1)–O(6)	77.8(1)	O(2)–Cu(2)–O(3)	94.1(1)
$O(2)-Cu(1)-O(8^{a})$	97.6(1)	$O(2)-Cu(2)-O(5^{b})$	93.8(1)
O(2)–Cu(1)–N(1)	90.3(1)	O(2)–Cu(2)–O(6)	79.5(1)

Table 6.4: Selected bond distances (Å) and angles (°) for 4[|](C₃₆H₆₀Cu₄MnN₁₀O₂₂)

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$O(6)-Cu(1)-N(8^{a})$	95.80(10)	O(3)–Cu(2)–	$-O(5^{b})$	93.3(1)
O(6)–Cu(1)–N(2)	90.2(1)	O(3)–Cu(2)–	-O(7)	90.3(1)
$O(8^{a})-Cu(1)-N(1)$	89.4(1)	$O(5^b)$ -Cu(2)	-O(6)	93.8(1)
$O(8^{a})-Cu(1)-N(2)$	95.3(1)	$O(5^b)$ -Cu(2)	-O(7)	99.8(1)
N(1)-Cu(1)-N(2)	100.6(1)	O(6)-Cu(2)-	-O(7)	94.4(1)
Cu(1)–O(2)–Cu(2)	100.8(1)	Cu(1)–O(6)–	-Cu(2)	101.5(1)
O(4)-Mn-O(9)	94.5(1)	O(4)–Mn–O	(9')	85.5(1)
O(4)-Mn-O(10)	96.7(1)	O(4)–Mn–O	(10')	83.3(1)
O(9)–Mn–O(10)	89.3(1)	O(9)–Mn–O	(10')	90.7(1)
а , , , ; ; ; ; ; ; ; ; ; ; ; ; ; ; ; ;	a . 1	1 b 1 c		1

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Symmetry operations: a - x, -y + 1, -z + 1, b - x, -y + 1, -z, b - x, -y, -z + 1.

Complex $4(C_{36}H_{54}Cu_4MnN_{10}O_{19})$ has a room-temperature magnetic moment of 6.32 μ_B that decreased with decreasing temperature to 5.58 μ_B at 2 K. Evidently an antiferromagnetic interaction operates between the adjacent Cu^{II} and Mn^{II} ions through the oximinato group, but it must be emphasized that the magnetic moment at 2 K is significantly low for $S_T = 5/2$ arising from an antiferromagnetic interaction within the pentanuclear CuCuMn–CuCu unit. It appears that an intermolecular antiferromagnetic interaction also occurs between the adjacent pentanuclear units, probably through the Cu2–O5^b–N2^b–Cu1^b pathway.^{28–31}

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