CHAPTER 6

Mononuclear and Heterometallic Dinuclear, Trinuclear and Dimer-of-Dinuclear Complexes Derived from Single- and Double-Compartment Schiff Base Ligands Having a Less Utilized Diamine

6.1. Introduction

Single-compartmental ligands that are the [2+1] condensation products of salicylaldehyde or 2-hydroxyacetophenone and a diamine as well as the double-compartmental ligands that are the [2+1] condensation products of 3-methoxysalicylaldehyde or 3-ethoxysalicylaldehyde or 3-hydroxysalicylaldehyde and a diamine are among the most studied ligand systems in coordination chemistry.[1] Several mononuclear and di-/tri-/oligonuclear systems as well as di/trinuclear-based polymeric systems are known.[1]

It is worth mentioning that both the above mentioned single-compartmental and double-compartmental ligands are potential to stabilize homo-/heteronuclear and di/tri/oligonuclear systems because of the presence of the two phenoxo oxygen atoms which can make bridges.[1] In fact, varieties of systems have been reported on isolating a copper(II)/nickel(II) mononuclear compound from a single-/double-compartmental ligand and then reacting that mononuclear compound with various second metal salts from different blocks of the periodic table. The second metal ion in those compounds include s-block metal ions (alkali and alkaline metal ions such as Li^{I}, Na^{I}, K^{I}, Rb^{I}, Cs^{I}, Mg^{II}, Ca^{II}, Sr^{II}, Ba^{II}),[2–13] p-block metal ions (such as Pb^{II}, Bi^{III}, Tl^{I}),[12,13,14–18] 3d-block metal ions (such as Cu^{II}, Ni^{II}, Co^{II}, Fe^{II}, Mn^{II}),[19–39] 4d/5d-block metal ions (such as Y^{III}),[40,41] d^{10} metal ions (such as Zn^{II}, Cd^{II}, Hg^{II}, Ag^{I}),[10,31,42–52] 4f metal ions (Ce^{III}–Yb^{III}) [40,53–74] and 5f metal ions (such as U^{VI}, ($U^{VI}O_2$).[75–81] Particular ligand and particular metal ion combinations are two major variables to stabilize different complexes. Again, the diamine counterpart and also the aldehyde counterpart are the variables to get different ligands. It is worth mentioning that the ligands having a diamine counterpart which has been only little used, deserves importance to get new types of systems in terms of metal ion combinations, new types of structures or in terms of getting interesting properties. In that perspective, 2,2-dimethyl-1,3-diaminopropane has been much less used in comparison to other diamines such as ethylenediamine, 1,3-diaminopropane, etc. There are only around 47 crystal structures of copper(II)/nickel(II)─second metal complexes derived from single-/double-compartmental ligands having 2,2-dimethyl-1,3-diaminopropane as the diamine counterpart.[7,8,22,23,28,31,40,41,46,48,57,58,60–70,74] Moreover,

most of (30) such complexes are 3d–4f systems.[57,58,60–70,74] Therefore, we have been motivated to explore copper(II)/nickel(II)–second metal ion complexes from single-/double-compartmental Schiff base ligands having 2,2-dimethyl-1,3-diaminopropane as the diamine counterpart. Accordingly, we have isolated two new mononuclear compounds $[Cu^{II}L^5]\cdot MeOH$ (**24**) and $[Ni^{II}L^5]$ and six heteronuclear complexes $[Cu^{II}(acetone)L^5(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$ (**25**), $[Cu^{II}(H_2O)L^7(U^{VI}O_2)(NO_3)_2]\cdot MeCN$ (**26**), $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**), $[\{Cu^{II}L^5Ag^{I}(NO_3)\}_2]$ (**28**), $[\{Cu^{II}L^6Ag^{I}(NO_3)\}_2]$ (**29**) and $[(Cu^{II}L^6)_2Cd^{II}(ClO_4)_2]$ (**30**), where H_2L^5, H_2L^6 and H_2L^7 are the [1+2] condensation products of 2,2-dimethyl-1,3-diaminopropane and, respectively, 2-hydroxyacetophenone (for H_2L^5), salicylaldehyde (for H_2L^6) and 3-ethoxysalicylaldehyde (for H_2L^7) (Chart 6.1). Herein we report the syntheses, characterization and diffuse reflectance spectra of these eight compounds and crystal structures of $[Cu^{II}L^5]\cdot MeOH$ (**24**) and **25**–**30**.

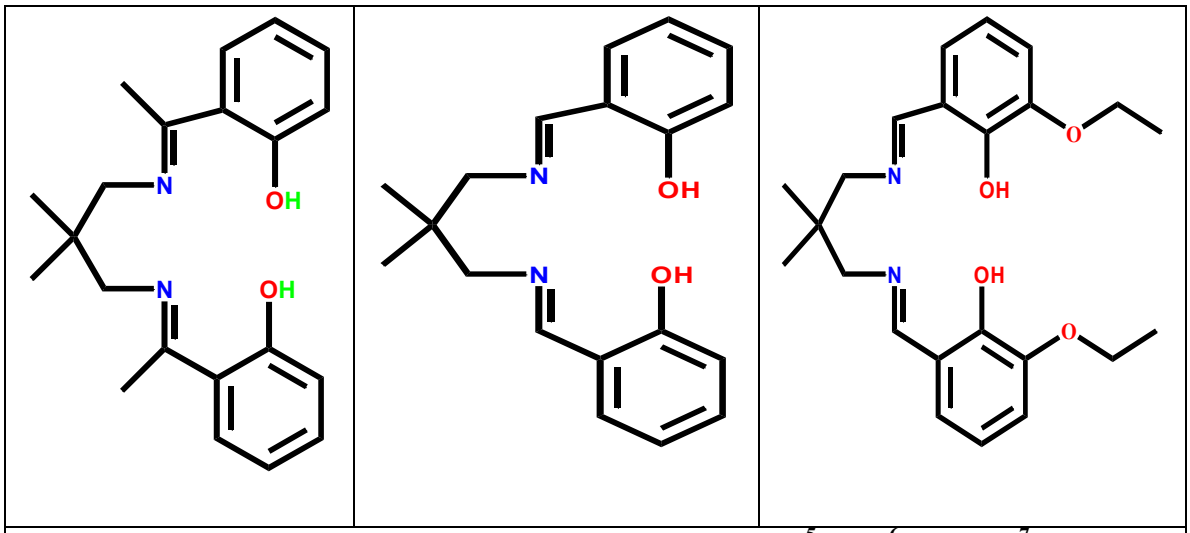

Chart 6.1. Chemical Structures of the ligands $\mathbf{H_2L^5}$, $\mathbf{H_2L^6}$ and $\mathbf{H_2L^7}$.

6.2. Experimental Section

6.2.1. Materials and Physical Measurements

All the reagents and solvents were purchased from commercial sources and used as received. The ligand H_2L^5,[82] H_2L^6[83] and H_2L^7[84]as well as the mononuclear compounds

$[Cu^{II}L^6]$ [85] and $[Cu^{II}L^7\supset(H_2O)]$[86] were synthesized by reported procedures. Elemental (C, H and N) analyses were performed on a Perkin-Elmer 2400 II analyzer. FT-IR spectra were recorded in the region 400–4000 cm^{-1} on a Bruker-Optics Alpha–T spectrophotometer with samples as KBr disks. Diffuse reflectance spectra of the solid compounds were recorded with a Hitachi U-3501 UV-Vis-NIR spectrophotometer using its integrating sphere set up.

6.2.2. Syntheses

$[Cu^{II}L^5]\cdot$MeOH (24). To a stirred suspension of H_2L^5 (0.338 g, 1.00 mmol) in MeOH (15 mL), was dropwise added a MeOH solution (5 mL) of copper(II) acetate monohydrate (0.200g, 1.00 mmol). After a few minutes a green compound started to deposit. The stirring was continued for 2 h and then the deposited solid was collected by filtration, washed with MeOH and air dried. Rerystallization was done from methanol solution to yield crystalline compound with diffraction quality single crystals.

$[Ni^{II}L^5]$. To a stirred suspension of H_2L^5 (0.338 g, 1.00 mmol) in MeOH (15 mL), was dropwise added a MeOH solution (5 mL) of nickel(II) acetate tetrahydrate (0.249g, 1.00 mmol). After a few minutes a brick red compound started to deposit. The stirring was continued for 2 h and then the deposited solid was collected by filtration, washed with MeOH and air dried. Rerystallization was done from methanol solution to yield crystalline compound.

$[Cu^{II}(acetone)L^5(U^{VI}O_2)(NO_3)_2]\cdot1.5CH_3COCH_3$ (25), $[Cu^{II}(H_2O)L^6(U^{VI}O_2)(NO_3)_2]\cdot$MeCN (26), and $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (27). These three compounds were prepared by following a general procedure, except using solvent and mononuclear starting materials as follows: (i) Acetone for **25** and **27**, 1:3 acetonitrile:acetone for **26**; (ii) $[Cu^{II}L^5]\cdot$MeOH for **25**, $[Cu^{II}L^7\supset(H_2O)]$ for **26** and $[Ni^{II}L^5]$ for **27**. As representative, synthesis procedure of **26** is described below:

A 1:3 acetonitrile:acetone solution (5 mL) of uranyl nitrate (0.063 g, 0.125 mmol) was dropwise added to a green suspension of $[Cu^{II}L^7\supset(H_2O)]$ (0.050 g, 0.105 mmol) in

the same solvent mixture (10 mL) with stirring. The color of the solution changes to reddish brown. The solution was filtered after a few minutes to remove any suspended particles. After 2–3 days, brown crystalline compound containing diffraction quality single crystals was collected by filtration and was washed with a 1:3 acetonitrile:acetone.

[{$Cu^{II}L^5Ag^I(NO_3)$}$_2$] (28) and [{$Cu^{II}L^6Ag^I(NO_3)$}$_2$] (29). These two compounds were prepared following similar procedures: To a suspension of corresponding mononuclear compound (0.050 g, 0.116/ 0.135 mmol; [$Cu^{II}L^5$]·MeOH for **28** and [$Cu^{II}L^6$] for **29**) in 10 mL MeOH, a MeOH solution (5 mL) of finely powdered silver(I) nitrate (0.050 g, 0.294 mmol) was added with stirring. The solution was filtered after a few minutes to remove any suspended particles. Crystalline compounds containing diffraction quality single crystals that deposited after 2–3 days from the filtered solution were collected by filtration and washed with MeOH.

[$(Cu^{II}L^6)_2Cd^{II}(ClO_4)_2$] (30). To a suspension of the [$Cu^{II}L^6$] (0.050 g, 0.135 mmol) in 10 mL methanol, a methanolic solution (5 mL) of finely powdered cadmium perchlorate.xH_2O (0.050 g, 0.160 mmol) was added with stirring. The solution was filtered after a few minutes to remove any suspended particles. Recrystallization on diffusing diethyl ether to the filtrate in a long tube yielded green crystalline compound containing diffraction quality single crystals.

6.2.3. Analytical and FT–IR Data

For **24**: Anal. Calcd for $C_{22}H_{28}N_2O_3Cu$: C, 61.16; H, 6.53; N, 6.48%. Found: C, 61.20; H, 6.25; N, 6.67%. FT-IR on KBr (cm^{-1}): ν(OH), 3385 m and 3286 w; ν(C=N), 1597 s.

For **[$Ni^{II}L^5$]**: Anal. Calcd for $C_{21}H_{24}N_2O_2Ni$: C, 63.83; H, 6.12; N, 7.09%. Found: C, 63.91; H, 5.78; N, 7.11%. FT-IR on KBr (cm^{-1}): ν(C=N), 1600 s.

For **25**: Anal. Calcd for $C_{24}H_{30}N_4O_{11}CuU$: C, 33.83; H, 3.54; N, 6.57%. Found: C, 33.67; H, 3.40; N, 6.45%. FT-IR on KBr (cm^{-1}): ν(C=O); acetone, 1706 s; ν(C=N), 1598 s; ν(nitrate), 1384 s and 1287 s; ν(uranyl), 932 m.

For **26**: Anal. Calcd for $C_{25}H_{33}N_5O_{13}CuU$: C, 32.88; H, 3.64; N, 7.67%. Found: C, 32.97; H, 3.75; N, 7.51%. FT-IR on KBr (cm^{-1}): ν(H_2O), 3475 s; ν(C=N), 1625 s; ν(nitrate), 1383 vs and 1275 s; ν(uranyl), 936 s.

For **27**: Anal. Calcd for $C_{24}H_{30}N_4O_{11}NiU$: C, 34.02; H, 3.57; N, 6.61%. Found: C, 33.88; H, 3.50; N, 6.70%. FT-IR on KBr (cm^{-1}): ν(C=O); acetone, 1706 s; ν(C=N), 1598 vs; ν (nitrate),1384 s and 1258 vs; ν(uranyl), 935 s.

For **28**: Anal. Calcd for $C_{42}H_{48}N_6O_{10}Cu_2Ag_2$: C, 44.26; H, 4.24; N, 7.37%. Found: C, 44.13; H, 4.35; N, 7.42%. FT-IR on KBr (cm^{-1}): ν(C=N), 1598 vs; ν(nitrate), 1321 s and 1234 s.

For **29**: Anal. Calcd for $C_{38}H_{40}N_6O_{10}Cu_2Ag_2$: C, 42.12; H, 3.72; N, 7.75%. Found: C, 42.10; H, 3.70; N, 7.69%. FT-IR on KBr (cm^{-1}): ν(C=N), 1623 vs; ν(nitrate), 1387 s and 1285 s.

For **30**: Anal. Calcd for $C_{38}H_{40}N_4O_{12}Cl_2Cu_2Cd$: C, 43.27; H, 3.82; N, 5.31%. Found: C, 43.40; H, 3.76; N, 5.20%. FT-IR on KBr (cm^{-1}): ν(C=N), 1623 s; ν(ClO_4), 1107 s and 620 m.

6.2.4. Crystal Structure Determination of 24–30

The crystallographic data for $[Cu^{II}L^5]\cdot MeOH$ (**24**) and the six compounds, **25**–**30**, are summarized in Table 6.1. Diffraction data of these seven compounds were collected on a Bruker-APEX II CCD diffractometer at 296 K using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). For data processing and absorption correction, the packages SAINT[88] and SADABS[88] were used. The structures were solved by direct and Fourier methods and refined by full-matrix least-squares based on F^2 using SHELXTL[89] and SHELXL-97 packages.[90]

During the development of the structures, it became apparent that few atoms in **25**–**30** were each disordered over two sites. These disordered atoms are as follows: C24 and O11 of coordinated acetone and O8 and O5 of one nitrate moiety in **25**; C8 of diimino side chain, C12 and C13 of ethoxy moiety, O7 of nitrate moiety in **26**; O6 of nitrate moiety in **27**; O3 and O4 of nitrate moiety in **28**; C8, C10 and C11 of diimino side chain, N1 of imine moiety, O6, O8 and O9 of nitrate moiety in **29**; O3, O5 and O6 of coordinated perchlorate moiety in **30**. The disorder was fixed allowing each individual atom to refine freely and the final occupancy parameters were set as: 0.90/0.10 for C8A/ C8B in **29**; 0.88/0.12 for C10A/C1OB in **29**; 0.86/0.14 for C11A/C11B in **29**; 0.80/0.20 for N1A/N1B in **29**; 0.75/0.25 for O8A/O8B in **29**; 0.70/0.30 for O11A/O11B in **1** and O4A/O4B in **28**; 0.65/0.35 for O8A/O8B in **25**; 0.60/0.40 for C24A/C24B in **25**, O6A/O6B in **27**, C12A/C12B and C13A/C13B in **26**, O9A/O9B in **29**, O3A/O3B and O5A/O5B in **30**; 0.50/0.50 for O5A/O5B in **25**, C8A/C8B and O7A/O7B in **26**, O3A/O3B in **28**, O6A/O6B in **29** and **30**.

It was understood during the solution of the structure of **25** that there were some acetone molecules as solvent of crystallization. However, it was not possible to assign them properly and therefore; the SQUEEZE facility of PLATON was utilized to omit this solvent molecule. [91] Electron count per unit cell for the eliminated solvent is 184, which is almost matched with one and half acetone molecules (electron count: calculated, 48; observed 46) per dinuclear unit ($Z = 4$). Therefore formula of this structure was set with one and half acetone molecules of crystallization.

The following hydrogen atom could not be located or inserted: One hydrogen atom of the hydroxyl group in the solvated MeOH molecule of $[Cu^{II}L^5]$·MeOH; Three hydrogen atoms of C15 (solvated acetonitrile) and two of coordinated water molecule (O2) in **26**; Two hydrogen atoms of each of the two disordered part C8A/C8B of the diimino side chain in **5**. All other hydrogen atoms in the seven compounds were inserted on geometrical calculated positions with fixed thermal parameters. All the hydrogen atoms, either located or inserted, were refined isotropically, while all the nonhydrogen atoms were refined anisotropically. The final least-squares refinements (R_1) based on $I > 2\sigma(I)$ converged to 0.0489, 0.0421, 0.0357, 0.0358, 0.0359, 0.0391, and 0.0383, respectively for $[Cu^{II}L^5]$·MeOH (**24**) and **25**–**30**.

Table 6.1. Crystallographic Data for **24**–**30**.

	24	**25**	**26**	**27**	**28**	**29**	**30**
empirical formula	$C_{22}H_{27}N_2O_3Cu$	$C_{24}H_{30}N_4O_{11}CuU$	$C_{25}H_{28}N_5O_{13}CuU$	$C_{24}H_{30}N_4O_{11}NiU$	$C_{21}H_{24}N_3O_5CuAg$	$C_{38}H_{38}N_6O_{10}Cu_2Ag_2$	$C_{38}H_{40}N_4O_{12}Cl_2Cu_2Cd$
fw	431.00	852.09	908.09	847.26	569.84	1081.56	1055.12
crystal system	triclinic	monoclinic	monoclinic	monoclinic	triclinic	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_1/n$	$C2/m$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$Pbca$
a (Å)	9.446(2)	10.5653(10)	17.6434(15)	11.5422(11)	8.7612(9)	11.7792(4)	12.2725(8)
b (Å)	10.112(2)	14.6023(13)	15.5819(13)	16.1131(16)	10.9070(11)	12.9690(5)	17.3638(12)
c (Å)	11.691(3)	22.793(2)	12.4084(9)	15.5319(15)	11.8649(13)	14.8805(6)	18.7769(12)
α (deg)	77.264(2)	90.00	90.00	90.00	97.051(5)	66.129(2)	90.00
β (deg)	85.193(2)	102.952(4)	108.492(3)	98.722(4)	108.009(5)	71.406(2)	90.00
γ (deg)	70.423(2)	90.00	90.00	90.00	105.316(5)	88.320(2)	90.00
V (Å^3)	1026.2(4)	3426.9(5)	3235.2(5)	2855.2(5)	1013.79(18)	1957.17(13)	4001.3(5)
Z	2	4	4	4	2	2	4
T (K)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)	296(2)
2θ (deg)	3.58–50.48	3.34–68.42	3.46–64.98	3.66–65.00	3.75–50.00	3.18–53.00	4.34–73.10
D_{calcd} (g cm^{-3})	1.395	1.652	1.864	1.971	1.867	1.835	1.751
F (000)	452	1644	1752	1640	574	1080	2128
Absorption-correction	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan	Multi-scan
Index ranges	$-9 \le h \le 11$	$-12 \le h \le 16$	$-26 \le h \le 26$	$-17 \le h \le 16$	$-10 \le h \le 10$	$-14 \le h \le 14$	$-14 \le h \le 20$
	$-11 \le k \le 12$	$-23 \le k \le 23$	$-23 \le k \le 20$	$-22 \le k \le 24$	$-12 \le k \le 12$	$-16 \le k \le 16$	$-28 \le k \le 29$
	$-13 \le l \le 13$	$-35 \le l \le 35$	$-18 \le l \le 16$	$-23 \le l \le 21$	$-14 \le l \le 14$	$-14 \le l \le 18$	$-27 \le l \le 31$
Independent reflections(R_{int})	3590 (0.0285)	13986(0.0497)	5970(0.0431)	10236(0.0466)	3508(0.0281)	7992(0.0257)	9802(0.0392)
Parameters refined	281	413	247	385	302	576	297
Goodness-of-fit on F^2	1.039	0.963	1.036	1.045	1.000	1.101	1.013
$R_1{}^a$ /w$R_2{}^b$ [$I > 2\sigma(I)$]	0.0489/0.1414	0.0421/0.0827	0.0357/0.0826	0.0358/0.0767	0.0359/ 0.1285	0.0391/0.1312	0.0383/0.1222
$R_1{}^a$ /w$R_2{}^b$ [for all F_o^2]	0.0609 /0.1570	0.0827/0.0906	0.0525/0.0909	0.0690/0.0872	0.0415/0.1365	0.0580/0.1592	0.0644/0.1414

[a] $R_1 = [\sum||F_o| - |F_c||/\sum|F_o|]$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^4]^{1/2}$

6.3. Results and Discussion

6.3.1. Description of Structures of $[Cu^{II}L^5]$·MeOH (24) and 25–30

Each of the mononuclear $[Cu^{II}L^5]$·MeOH (**24)** (Figure. 6.1) and heterometallic compounds $[Cu^{II}(acetone)L^5(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$ (**25**; Figure 6.2), $[Cu^{II}(H_2O)L^7(U^{VI}O_2)(NO_3)_2]$·MeCN (**26**; Figure 6.3), $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**; Figure 6.4), $[\{Cu^{II}L^5Ag^{I}(NO_3)\}_2]$ (**28**; Figure 6.5), $[\{Cu^{II}L^6Ag^{I}(NO_3)\}_2]$ (**29**; Figure 6.6) and $[(Cu^{II}L^6)_2Cd^{II}(ClO_4)_2]$ (**30**; Figure 6.7), contain one or more number of diprotonated single-compartment Schiff base ligand, $[L^5]^{2-}$ (for **24**, **25**, **27**, and **28**), $[L^6]^{2-}$ (for **29** and **30**) and $[L^7]^{2-}$ (for **26**). A common feature of these compounds is that the $N(imine)_2O(phenoxo)_2$ compartment of the Schiff base ligands is occupied by Cu^{II} (for $[Cu^{II}L^5]$·MeOH (**24**), **25**, **26**, **28**, **29** and **30**) or Ni^{II} (for **27**). Among these metal ions in the $N(imine)_2O(phenoxo)_2$ compartment, copper(II) in $[Cu^{II}L^5]$·MeOH, **28**, and nickel(II) in **27** are tetracoordinated, while copper(II) in **25**, **26**, **29**, and **30** is pentacoordinated due to the additional coordination by an acetone oxygen atom in **25**, an water oxygen atom in **26**, a nitrate oxygen atom in **29** (semicoordianted), and a perchlorate oxygen atom in **30**. The other aspects of the structures are discussed below in three sections for the sake of simplicity.

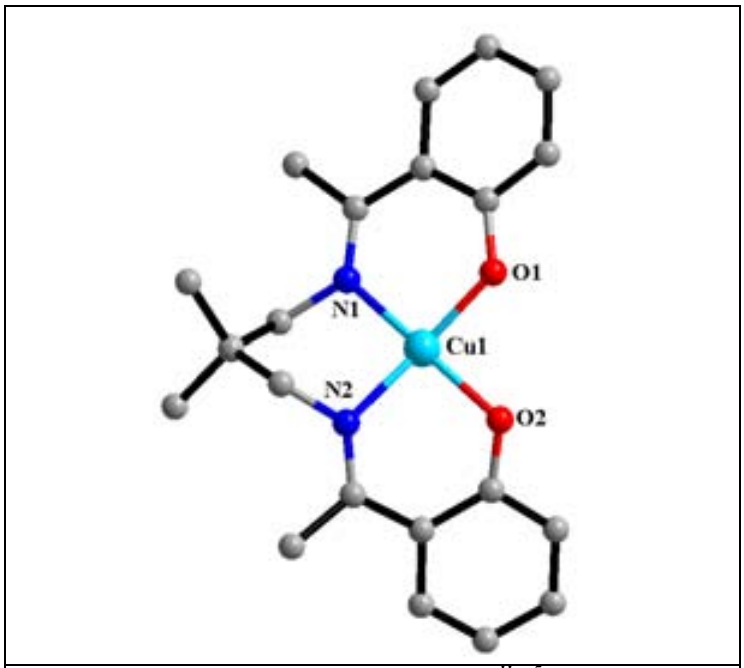

Figure 6.1. Crystal structure of $[Cu^{II}L^{5}]\cdot MeOH$ (**24**). All the hydrogen atoms and the solvated methanol molecule have been omitted for clarity.

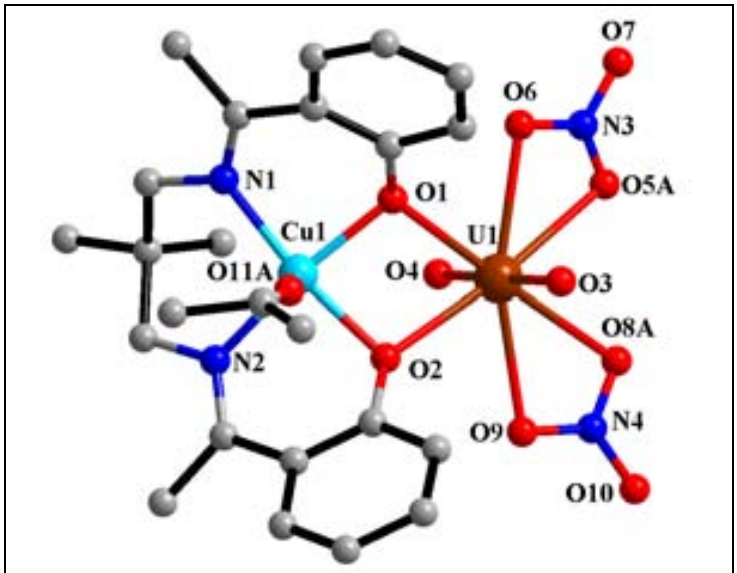

Figure 6.2. Crystal structure of $[Cu^{II}(acetone)L^{5}(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$(**25**). All the hydrogen atoms and the solvated acetone molecules are omitted for clarity.

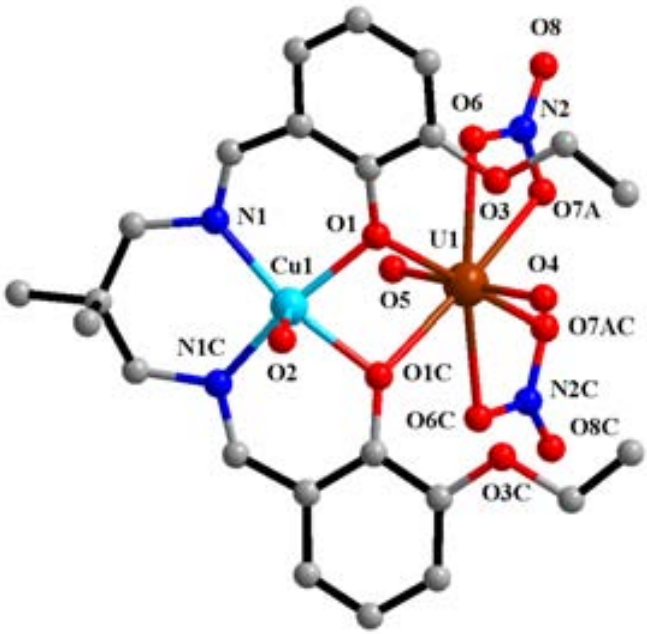

Figure 6.3. Crystal structure of $[Cu^{II}(H_2O)L^7(U^{VI}O_2)(NO_3)_2]\cdot MeCN$ (**26**). All the hydrogen atoms and the solvated acetonitrile molecule are omitted for clarity. Symmetry: C, x, –y, z.

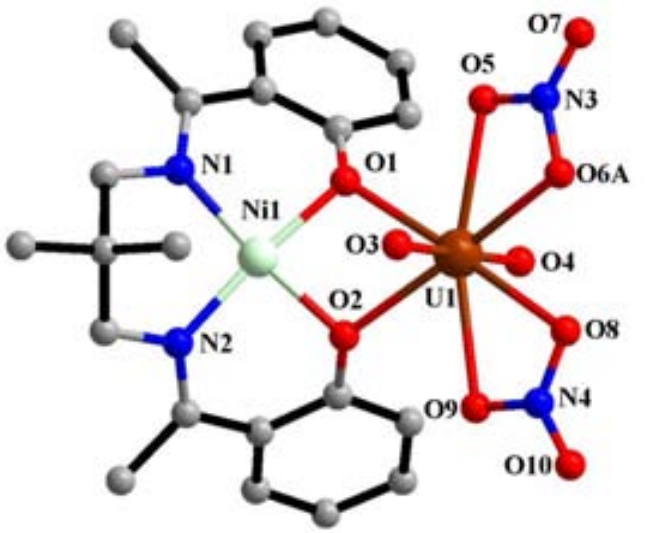

Figure 6.4. Crystal structure of $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**). All the hydrogen atoms and the solvated acetone molecule are omitted for clarity.

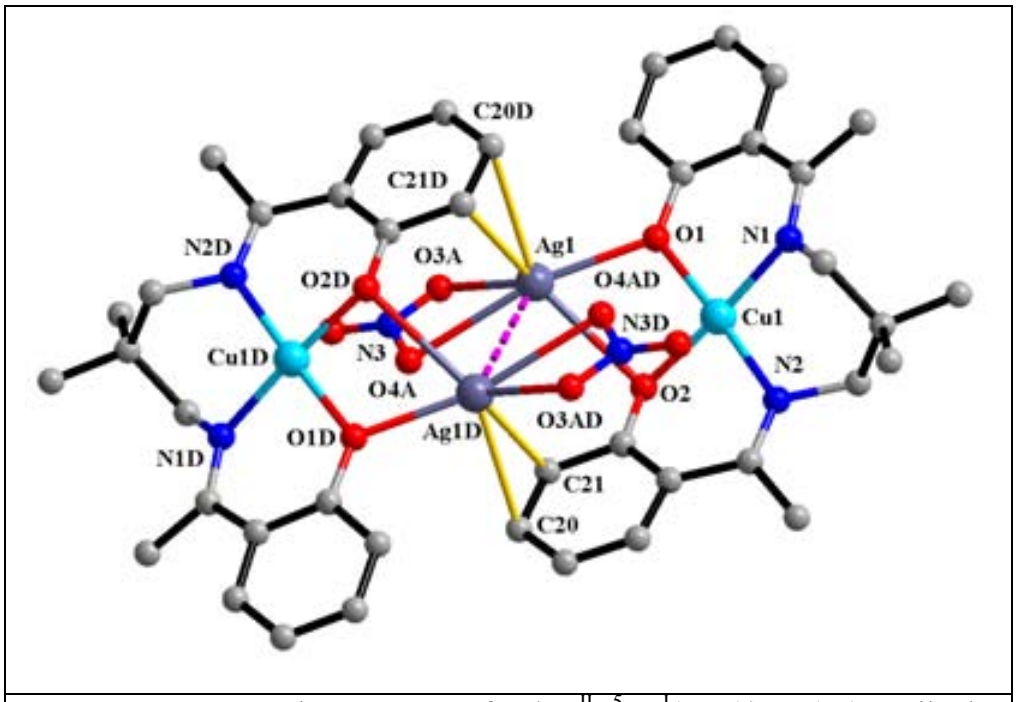

Figure. **6.5**. Crystal structure of [{$Cu^{II}L^{5}Ag^{I}(NO_3)$}$_2$] (**28**). All the hydrogen atoms are omitted for clarity. Symmetry: D, 1–x, 2–y, 1–z.

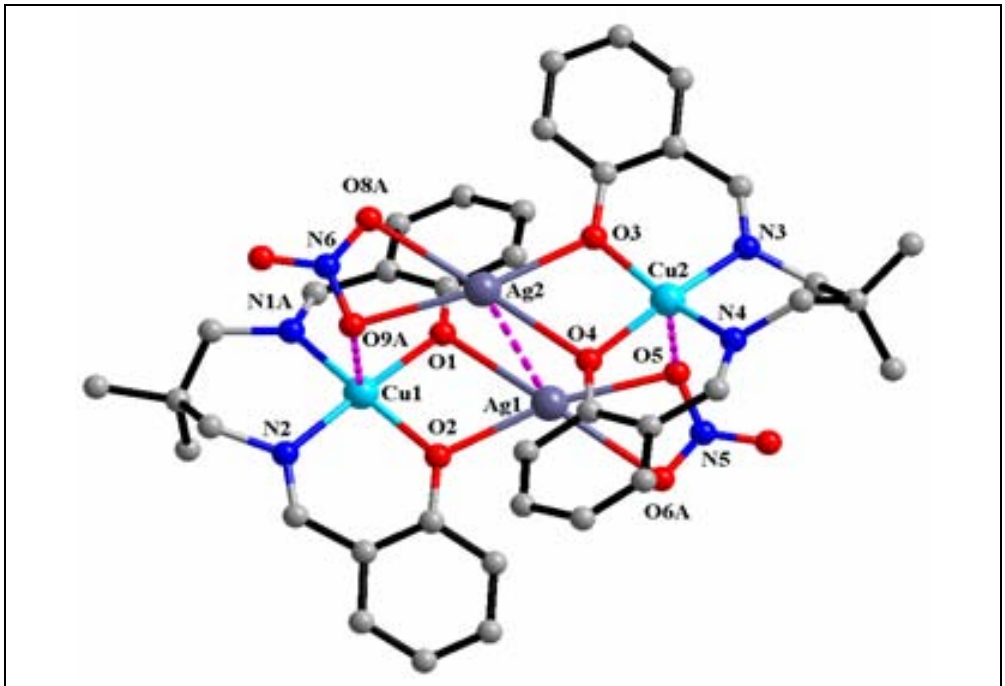

Figure. **6.6**. Crystal structure of [{$Cu^{II}L^{6}Ag^{I}(NO_3)$}$_2$] (**29**). All the hydrogen atoms are omitted for clarity.

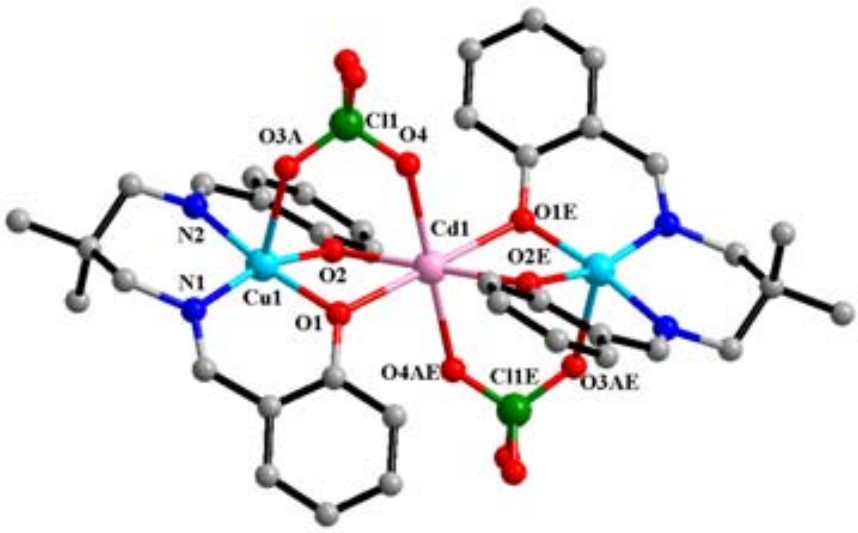

Figure. **6.7**. Crystal structure of $[(Cu^{II}L^{6})_2Cd^{II}(ClO_4)_2]$(**30**). All the hydrogen atoms are omitted for clarity. Symmetry: E, 1–x, 1–y, 1–z.

Types of Structures. As already mentioned, $[Cu^{II}L^{5}]$·MeOH (Figure 6.1) is a mononuclear compound. On the other hand, the three compounds of composition $[Cu^{II}(acetone)L^{5}(U^{VI}O_2)(NO_3)_2]$·$1.5CH_3COCH_3$ (**25**; Figure 6.2), $[Cu^{II}(H_2O)L^{7}(U^{VI}O_2)(NO_3)_2]$·MeCN (**26**; Figure 6.3) and $[Ni^{II}L^{5}(U^{VI}O_2)(NO_3)_2]$·$CH_3COCH_3$ (**27**; Figure 6.4) are diphenoxo-bridged copper(II)–uranyl(VI) (**25** and **26**) / nickel(II)–uranyl(VI) (**27**) systems. The uranyl(VI) center in all these three compounds is coordinated to the two bridging phenoxo oxygen atoms, two uranyl oxygen atoms and two oxygen atoms of each of the two chelating nitrate ligands. This way, uranyl(VI) center in **25**–**27** is octacoordinated. Copper(II)/nickel(II) and uranium(VI) centers in **25**–**27** reside at opposite directions with respect to the O(phenoxo)····O(phenoxo) line. In **25** and **26**, copper(II) and uranium(VI) centers are displaced to opposite directions from the least-squares $N(imine)_2O(phenoxo)_2$ plane (displacement values for copper(II) and uranium(VI) are +0.133 and –1.178 Å in **25** and –0.215 and +1.681Å in **26**; Table 6.2). On the other hand, the nickel(II) center in **27** is practically lie on the least-squares $N(imine)_2O(phenoxo)_2$ plane (displacement value is only +0.010 Å) and the uranium(VI) center from this plane is displaced by +1.188 Å.

$[\{Cu^{II}L^{5}Ag^{I}(NO_3)\}_2]$ (**28**; Figure 6.5), $[\{Cu^{II}L^{6}Ag^{I}(NO_3)\}_2]$ (**29**; Figure 6.6) are dimer-of-dinuclear type tetranuclear $[Cu^{II}Ag^{I}]_2$ systems. In the dinuclear unit of both **28** and **29**, copper(II) and silver(I) are diphenoxo-bridged. One bidentate chelating nitrate is also coordinated to the silver(I) center. One dinuclear $[Cu^{II}L^{5/6}Ag^{I}(NO_3)]$ unit in both **28** and **29** are interlinked with a neighboring unit (symmetry related in **28**; crystallographically different in **29**) to form the dimer-of-dinuclear type structure. However, the nature of interactions responsible for interlinking is different in the two compounds. In **29**, two types of interactions are responsible: (i) One nitrate oxygen atom (coordinated to silver(I)) of a dinuclear unit becomes semicoordinated with the copper(II) center of a second dinuclear unit; (ii) Silver(I)····silver(I) interaction. In **28**, two types of interactions are responsible: (i) Silver(I) of one dinuclear unit is coordinated to an arene ring of a second dinuclear unit in η^2-mode; (ii) Silver(I)····silver(I) interaction. With respect to the least-squares $N(imine)_2O(phenoxo)_2$ plane, displacement of copper(II) in both **28** and **29** is small (–0.050 and +0.074 / –0.105Å, respectively; Table 6.2). However, from this plane, displacement value of silver(I) in **28** (+1.130; Table 6.2) is much greater than that in **29** (–0.185 / +0.4308 Å; Table 6.2).

$[(Cu^{II}L^{6})_2Cd^{II}(ClO_4)_2]$ (**30**; Figure 6.7) is a trinuclear $Cu^{II}Cd^{II}Cu^{II}$ system in which the cadmium(II) center resides in between two symmetry related $[Cu^{II}L^{6}]$ units and is coordinated to all the four phenoxo oxygen atoms, i.e., copper(II) and cadmium(II) centers are diphenoxo bridged. Copper(II) and cadmium(II) centers are further bridged by the two oxygen atoms of a $\mu_{1,3}$–perchlorate ligand. This way, cadmium(II) center is hexacoordinated by four bridging phenoxo and two $\mu_{1,3}$-perchlorate oxygen atoms. The arrangement of the three metal centers Cu1, Cd1 and Cu1E is linear (Cu1···Cd1···Cu1E angle is 180°). With respect to the least-squares $N(imine)_2O(phenoxo)_2$ plane, displacement of copper(II) and cadmium(II) in **30** occurs towards the same direction. However, displacement of copper(II) is much smaller, –0.116 Å, than that of cadmium(II), –0.631 Å.

Table 6.2. Some Structural Parameters (Distances in Å and Angles in deg) in **24**–**30**.

	24	**25**	**26**	**27**	**28**	**29**	**30**
Cu/Ni–phenoxo	1.863, 1.897	1.945, 1.951	1.969, 1.969	1.867, 1.869	1.913, 1.925	1.928, 1.932 / 1.916, 1.917[d]	1.938, 1.964
Cu/Ni–imine	1.962, 1.966	1.946, 1.969	1.970, 1.970	1.883, 1.883	1.973, 1.987	1.955, 2.016 / 1.939, 1.944 [d]	1.967, 1.969
Cu–apical ligand	—	2.440	2.363	—	—	2.655 / 2.749 [d]	—
Cisoid angles	88.11–93.93	82.18–97.49	78.17–101.32	83.55–95.13	87.68–92.94	83.03–99.72 / 82.70–96.32 [d]	82.27–100.5
Transoid angles	155.65, 165.64	167.31, 170.42	164.94, 164.94	174.02, 174.26	175.65, 176.44	163.70, 171.49 / 154.71, 162.17 [d]	161.25, 172.47
τ	—	0.052	0.00	—	—	0.124 / 0.130 [d]	0.187
$d_{N/O}$[a]	0.318	0.044	0.00	0.011	0.002	0.180 / 0.314 [d]	0.176
$d_{Cu/Ni}$ [a]	+0.076	+0.133	–0.215	+0.010	–0.050	+0.074 / –0.105 [d]	–0.116
$d_M(N_2O_2)$[a]	—	–1.178	+1.681	+1.188	+1.130	–0.185 / +0.438 [d]	–0.631
U–phenoxo		2.399, 2.412	2.431	2.428, 2.441	—	—	—
U=O	—	1.763, 1.764	1.756,1.766	1.757, 1.757	—	—	—
U–nitrate		2.499–2.620	2.492–2.522	2.426–2.505	—	—	—
Ag–phenoxo	—	—	—	—	2.289, 2.683	2.331–2.427	—
Ag–nitrate	—	—	—	—	2.300, 2.639	2.413–2.527	—
Ag–C (η^2)	—	—	—	—	2.692, 2.784	—	—
Ag···Ag interaction	—	—	—	—	3.346	3.283	—
Cd–phenoxo	—	—	—	—	—	—	2.257, 2.243
Cd–perchlorate	—	—	—	—	—	—	2.368
Cu···M distance	—	3.386	3.345	3.331	3.361	3.390 / 3.445 [d]	3.240
O–Ag–O	—	—	—	—	44.9– 165.6	50.9–173.7	—
O–U–O							
180° set	—	162.09–178.45	157.9–176.11	163.14–179.28	—	—	—
120° set	—	112.60–131.60	108.4–130.4	112.1–129.53	—	—	—
90° set	—	84.00–95.90	84.40–95.73	84.10–95.2	—	—	—
60° set	—	47.00–67.69	50.60–69.26	50.32–68.16	—	—	—
Cisoid O–Cd–O	—	—	—	—	—	—	69.58–110.42
Transoid O–Cd–O	—	—	—	—	—	—	180.00
d_U/ d_{Cd}[b]		0.008	0.175	0.059	—	—	0.000
d_O[b]	—	0.115	0.005	0.102	—	—	0.000
δ_{arene}[c]	45.76	85.03	22.47	82.09	10.49	45.13 / 40.23	59.72

[a] $d_{Cu/Ni}$ is the displacement of the Cu^{II}/Ni^{II} center, $d_M(N_2O_2)$ is the displacement of the U^{VI} (in **25**–**27**) / Ag^{I} (in **28** and **29**) / Cd^{II} (in **30**) and $d_{N/O}$ is the average deviation of the constituent atoms from the corresponding least-squares $N(imine)_2O(phenoxo)_2$ plane. [b] d_U/ d_{Cd} is the displacement of the U^{VI} (in **25**–**27**) / Cd^{II} (in **30**) and d_O is the average deviation of the constituent atoms from the least-squares O_5 (in **25**–**27**) / O_4 (in **30**) basal plane. [c] Dihedral angle between two arene rings. [d] Two types of Cu^{II} centers.

Structural Parameters and Coordination Geometry. Selected structural parameters of $[Cu^{II}L^5]$·MeOH (**24**) and **25**–**30** are summarized in Table 6.2, while the individual bond lengths and bond angles for $[Cu^{II}L^5]$·MeOH (**24**) and **25**–**30** are listed in Table 6.3–6.9 for $[Cu^{II}L^5]$·MeOH (**24**) and **25**–**30** respectively.

The U^{VI}–O(phenoxo) bond distances in **25** (2.399 and 2.412 Å) and **26** (2.431 Å) are clearly shorter than the U^{VI}–O(nitrate) bond distances (2.499–2.620 Å in **25**; 2.492–2.522 Å in **26**), while the U^{VI}–O(phenoxo) bond distances in **27** (2.428 and 2.441 Å) are within the range of the U^{VI}–O(nitrate) bond distances (2.426–2.505 Å). On the other hand, as expected, U^{VI}–O(uranyl) bond distances (1.763 and 1.764 Å in **25**; 1.756 and 1.766 Å in **26**; 1.757 Å in **27**) are significantly shorter than both the U^{VI}–O(phenoxo) and U^{VI}–O(nitrate) bond distances. The uranium(VI) center in each compound is octacoordinated and adopts a distorted hexagonal bipyramidal coordination geometry in which the two uranyl oxygen atoms occupy the axial positions. Both the displacement (d_U = 0.008, 0.175, and 0.059 Å in **25**–**27**, respectively) of the uranium(VI) center and average deviation (d_O = 0.115, 0.005, and 0.102 Å in **25**–**27**, respectively) of the constituent six oxygen atoms from the least-squares O_6 hexagonal basal plane are rather small. However, the deviation of the O–U–O bond angles from the ideal values is significant in all the three compounds and the deviation of each of the four sets (180°, 120°, 90° and 60°) of O–U–O bond angles in all the three complexes follow a general trend. The significant deviation of O–U–O bond angles and the wide range of U–O bond distances (1.763–2.620 Å in **25**; 1.756–2.522 Å in **26**; 1.757–2.505 Å in **27**) indicate that the geometry of the uranium(VI) center in **25**–**27** is significantly distorted. The Schiff base ligand part in **25** and **27** is significantly twisted in comparison to that in **26**, as evidenced from the dihedral angle between the two arene rings (85.03°, 82.09° and 22.47 °in **25**, **27** and **26**, respectively).

Two Ag^I–O(phenoxo) bond distances are 2.289 and 2.683 Å in **28** and 2.331–2.427 Å in **29**. Clearly, two Ag^I–O(phenoxo) bond distances in **28** is more asymmetric (asymmetry = 0.394) than in **29** (asymmetry = 0.071/0.088). The coordinating nitrate oxygen atoms in both **28** and **29** are disordered and so comparison of the Ag^I–O(nitrate) bond distances (2.300 and 2.639 Å in **28**; 2.413–2.527 Å in **29**) may be not realistic. Still,

as is observed in the two Ag^{I}–O(phenoxo) bond distances, two Ag^{I}–O(nitrate) bond distances in **28** are significantly asymmetric (asymmetry = 0.339), while those in **29** are much less asymmetric (asymmetry = 0.004/0.114). Ag^{I}–C (η^2) bond distances in **28** are 2.692 and 2.784 Å. $Ag^{I}\cdots Ag^{I}$ distance in **28** and **29** is 3.346 and 3.283Å, respectively. The Schiff base ligand part is more twisted in **29** than that in **28**, as evidenced from the dihedral angle between the two arene rings (10.49 and 45.13/40.23 in **28** and **29**, respectively).

The two types of Cd^{II}–O(phenoxo) bond distances in **30** are 2.257 and 2.243 Å, while one type of Cd^{II}–O(perchlorate) bond distance (2.368 Å) in this compound is greater than the Cd^{II}–O(phenoxo) bond distances. The $Cd^{II}O_6$ coordination environment in **30** is distorted octahedral. The following parameters apparently may indicate that the distortion in the coordination environment is small: (i) All the three *transoid* angles are 180°; (ii) All the three possible basal planes are perfect planes (deviation of constituent atoms from the corresponding least-squares O_4 plane is zero) and cadmium(II) center lies on all the three possible O_4 planes. However, wide ranges of *cisoid* angles (69.58–110.42°) indicate that the coordination geometry is in fact significantly distorted. The Schiff base ligand part is significantly twisted in **30**, as evidenced from the dihedral angle between the two arene rings (59.72°). However, not only that the arrangement of the three metal ions (Cu1, Cd1, Cu1E) is linear but also the two least-squares basal $N(imine)_2O(phenoxo)_2$ planes of the two copper(II) centers belong are the same plane.

The structural parameters involving copper(II)/nickel(II) in $[Cu^{II}L^5]\cdot MeOH$ (**24**) and **25**–**30** are also listed in Table 6.2. The coordination geometry of the copper(II) center in $[Cu^{II}L^5]\cdot MeOH$(**24**), **28** and **29** and nickel(II) center in **27** is distorted square planer, while that of the copper(II) center in **25**, **26**, **29**, and **30** is distorted square pyramidal, where $N(imine)_2O(phenoxo)_2$ defines the basal plane. Two copper(II)/nickel(II)–O(phenoxo) and two copper(II)/nickel(II)–N(imine) bond distances are very close in some cases, while clearly different in some other cases. In comparison to basal copper(II)– N(imine)/ O(phenoxo) bond distances, the apical copper(II)–O(acetone)/O(water)/O(perchlorate) bond distances are significantly longer as expected due to Jahn-Teller distortion. As listed in Table 6.2, the *cisoid* and *transoid* angles

indicates distorted square planar or square pyramidal coordination geometry of copper(II) nickel(II) in $[Cu^{II}L^5]$·MeOH (**24**) and **25**–**30**.

Table 6.3. Selected Bond Lengths (Å) and Angles (deg) of $[Cu^{II}L^5]$·MeOH (**24**).

Cu1–O1	1.863(3)
Cu1–O2	1.897(3)
Cu1–N1	1.966(3)
Cu1–N2	1.962(3)
O1–Cu1–N2	155.65(14)
O2–Cu1–N1	165.64(14)
O1–Cu1–N1	93.93(13)
N2–Cu1–N1	93.44(13)
N2–Cu1–O2	90.49(12)
O1–Cu1–O2	88.11(12)

Table 6.4. Selected Bond Lengths (Å) and Bond Angles (deg) in the Coordination Environment Copper(II) and Uranium(VI) Centers in **25**.

Bond lengths		**Bond Angles**			
Cu(II) center		Cu(II) center		U(VI) center	
Cu1–N1	1.946(2)	O1–Cu1–N2	167.31(9)	O3–U1–O4	178.45(10)
Cu1–N2	1.969(2)	O2–Cu1–N1	170.42(10)	O2–U1–O5A	171.1 (7)
Cu1–O1	1.951(2)	O1–Cu1–O2	82.18(9)	O1–U1–O8A	176.0(4)
Cu1–O2	1.945(2)	O1–Cu1–N1	89.36(10)	O6–U1–O9	162.09(8)
Cu1–O11A	2.440(12)	O2–Cu1–N2	90.02(10)	O1–U1–O9	131.60(7)
		N1–Cu1–N2	97.49(11)	O1–U1–O5A	112.60(5)
U(VI) center		O11A–Cu1–N1	93.51(28)	O2–U1–O8A	116.60(4)
U1–O1	2.412(2)	O11A–Cu1–N2	97.03(28)	O2–U1–O6	130.11(7)
U1–O2	2.399(2)	O11A–Cu1–O1	93.18(28)	O6–U1–O8A	113.3(4)
U1–O3	1.764(2)	O11A–Cu1–O2	91.49(28)	O5A–U1–O9	115.8 (5)
U1–O4	1.763(2)			O3–U1–O5A	92.6(8)
U1–O5A	2.620(2)	Cu1–O1–U1	101.31(8)	O3–U1–O6	89.04(10)
U1–O6	2.499(4)	Cu1–O2–U1	101.94(8)	O3–U1–O9	86.59(9)
U1–O8A	2.540(2)			O3–U1–O8A	84.0(4)
U1–O9	2.504(3)			O4–U1–O5A	86.1(8)
				O4–U1–O6	90.53(10)
Cu1···U1	3.3866(5)			O4–U1–O9	93.38(9)
				O4–U1–O8A	94.8(4)
				O2–U1–O3	95.90(10)
				O2–U1–O4	85.52(10)
				O1–U1–O3	92.09(9)
				O1–U1–O4	89.09(9)
				O5A–U1–O6	47.0 (5)
				O5A–U1–O8A	67.1(6)
				O8A–U1–O9	49.0(4)
				O1–U1–O2	64.34(6)
				O1–U1–O6	65.89(7)
				O2–U1–O9	67.69(7)

Table 6.5. Selected Bond Lengths (Å) and Bond Angles (deg) in the Coordination Environment of the Copper(II) and Uranium(VI) Centers in **26**. Symmetries are as in Figures.

Bond lengths		**Bond Angles**			
Cu(II) center		Cu(II) center		U(VI) center	
Cu1–N1	1.970(3)	O1–Cu1–N1C	164.94(13)	O4–U1–O5	176.11(18)
Cu1–N1C	1.970(3)	O1C–Cu1–N1	164.94(13)	O1–U1–O7AC	171. 8(2)
Cu1–O1	1.969(3)	O1–Cu1–O1C	78.17(13)	O6–U1–O6C	157.90(10)
Cu1–O1C	1.969(3)	O1–Cu1–N1	92.21(12)	O1C–U1–O7A	171.8(2)
Cu1–O2	2.363(4)	O1C–Cu1–N1C	92.21(12)	O1–U1–O6C	130.41(8)
		N1C–Cu1–N1	94.64(19)	O1–U1–O7A	119.7(3)
U(VI) center		O2–Cu1–N1	101.32(14)	O6–U1–O7AC	108.4 (2)
U1–O1	2.431(2)	O2–Cu1–N1C	101.32(14)	O1C–U1–O6	130.41(8)
U1–O1C	2.431(2)	O2–Cu1–O1	90.43(13)	O1–U1–O7AC	119.7(3)
U1–O4	1.756(4)	O2–Cu1– O1C	90.43(13)	O6C–U1–O7A	108.4 (2)
U1–O5	1.766(4)			O1–U1–O4	95.73(12)
U1–O6	2.522(3)	Cu1–O1–U1	98.42(9)	O1–U1–O5	87.61(13)
U1–O7A	2.492(8)	Cu1–O1C–U1	98.42(9)	O4–U1–O6	93.79(7)
U1–O6C	2.522(3)			O4–U1–O7A	92.2(2)
U1–O7AC	2.492(8)			O5–U1–O6	85.51(7)
				O5–U1–O7A	84.4 (2)
Cu1···U1	3.3455(6)			O1C–U1–O4	95.73(12)
				O1C–U1–O5	87.61(13)
				O4–U1–O6C	93.79(7)
				O4–U1–O7AC	92.2(2)
				O5–U1–O6C	85.51(7)
				O5–U1–O7AC	84.4 (2)
				O1–U1–O1C	61.42(11)
				O1–U1–O6	69.25(8)
				O6–U1–O7A	50.6(3)
				O7A–U1–O7AC	57.9 (5)
				O1C–U1–O6C	69.26(8)
				O7AC–U1–O6C	50.6(3)

Table 6.6. Selected Bond Lengths (Å) and Bond Angles (deg) in the Coordination Environment of the Nickel(II) and Uranium(VI) Centers in **27**.

Bond lengths		**Bond Angles**			
Ni(II) center		Ni(II) center		U(VI) center	
Ni1 –N2	1.883(3)	O1– Ni1–N2	174.02(12)	O1–U1–O8	175.39(9)
Ni1 –N1	1.883(3)	O2– Ni1–N1	174.26(11)	O2–U1–O6A	171.6(4)
Ni1–O2	1.869(2)	O1– Ni1–O2	83.55(10)	O5–U1–O9	163.14(10)
Ni1–O1	1.867(2)	O2– Ni1–N2	90.60(11)	O3–U1–O4	179.28(13)
		O1– Ni1–N1	90.72(11)	O1–U1–O6A	118.9 (5)
U(VI) center		N1– Ni1–N2	95.13(12)	O1–U1–O9	128.42(9)
U1–O1	2.428(2)			O2–U1–O5	129.53(9)
U1–O2	2.441(2)	Ni1–O1–U1	100.87(10)	O2–U1–O8	117.02(9)
U1–O3	1.757(3)	Ni1–O2–U1	100.39(10)	O5–U1–O8	113.44(10)
U1–O4	1.757(3)			O6A–U1–O9	112.1(5)
U1–O5	2.498(3)			O1–U1–O3	86.48(18)
U1–O6A	2.426(19)			O1–U1–O4	93.65(11)
U1–O8	2.496(3)			O2–U1–O3	87.61(11)
U1–O9	2.505(3)			O2–U1–O4	93.08(10)
				O5–U1–O3	92.56(12)
Ni1···U1	3.3307(5)			O5–U1–O4	86.84(12)
				O6A–U1–O3	84.1(4)
				O6A–U1–O4	95.2(5)
				O8–U1–O3	89.10(12)
				O8–U1–O4	90.78(12)
				O9–U1–O3	91.71(12)
				O9–U1–O4	88.76(12)
				O2–U1–O1	61.48(8)
				O2–U1–O9	66.94(9)
				O5–U1–O6A	52.3(5)
				O5–U1–O1	68.16(9)
				O8–U1–O6A	61.8(5)
				O8–U1–O9	50.32(9)

Table 6.7. Structural Parameters (Distances in Å and Angles in deg) in the Coordination Environment of Copper(II) and Silver(I) Centers in **28**. Symmetries are as in Figures.

Bond lengths		**Bond Angles**			
Cu(II) center		Cu(II) center		Ag(I) center	
Cu1–N1	1.987(3)	N1–Cu1–O2	175.65(13)	O1– Ag1–O2	64.07(9)
Cu1–N2	1.973(3)	N2–Cu1–O1	176.44(12)	O2–Ag1–O4A	103.90(5)
Cu1–O2	1.925(3)	N1–Cu1–N2	92.94(13)	O4A–Ag1–O3A	44.9(7)
Cu1–O1	1.913(3)	N1–Cu1–O1	89.13(12)	O3A–Ag1–O1	132.4(6)
		N2–Cu1–O2	90.10(13)	O2–Ag1–O3A	119.40(9)
Ag (I) center		O1–Cu1–O2	87.68(12)	O1–Ag1–O4A	165.60(4)
Ag1–O1	2.289(3)			O1–Ag1–C20D	89.07(13)
Ag1–O2	2.683(3)	Cu1–O1–Ag1	105.90(12)	O1–Ag1–C21D	107.74(12)
Ag1–O3A	2.30(4)	Cu1–O2–Ag1	92.17(12)	O2–Ag1–C20D	143.79(12)
Ag1–O4A	2.639(14)			O2–Ag1–C21D	134.81(11)
Ag1–C20D	2.784(5)			O3A–Ag1–C20D	96.45(80)
Ag1–C21D	2.692(4)			O3A–Ag1–C21D	99.0(9)
Ag1···Ag1D	3.3464(9)			O4A–Ag1–C20D	105.00(44)
				O4A–Ag1–C21D	86.3 (4)
Cu1···Ag1	3.3612(8)			C20D– Ag1–C21D	29.35(14)

Table 6.8. Structural Parameters (Distances in Å and Angles in deg) in the Coordination Environment of Copper(II) and Silver(I) Centers in **29**.

Bond lengths		**Bond Angles**			
Cu(II) center		Cu(II) center		Ag(I) center	
Cu1–N1A	2.016(4)	N1A–Cu1–O2	163.70(17)	O1– Ag1–O2	65.16(9)
Cu1–N2	1.955(3)	N2–Cu1–O1	171.49(12)	O1–Ag1–O6A	173.6(5)
Cu1–O2	1.928(3)	N1A–Cu1–N2	95.32(15)	O1–Ag1–O5	128.13(10)
Cu1–O1	1.932(2)	N1A–Cu1–O1	91.16(15)	O2–Ag1–O5	166.70(10)
Cu1–O9A	2.655(15)	N2–Cu1–O2	92.12(13)	O2–Ag1–O6A	115.7(4)
Cu2–N3	1.944(3)	O1–Cu1–O2	83.03(12)	O5–Ag1–O6A	51.2(4)
Cu2–N4	1.939(3)	O9A–Cu1–O1	86.36(31)	O4– Ag2– O8A	173.7(3)
Cu2–O3	1.916(3)	O9A–Cu1–O2	99.72(33)	O3– Ag2– O9A	166.2(2)
Cu2–O4	1.917(2)	O9A–Cu1–N2	87.60(31)	O3 –Ag2– O4	66.48(9)
Cu2– O5	2.749(4)	O9A–Cu1–N1A	95.08(37)	O4– Ag2 –O9A	125.9(2)
		N3–Cu2–O4	162.17(13)	O8A–Ag2– O9A	50.9(4)
Cu1···Ag1	3.4455(7)	N4–Cu2–O3	154.71(15)	O3– Ag2 –O8A	117.5(3)
Cu2···Ag2	3.3898(7)	N3–Cu2–N4	92.07(13)		
		N4–Cu2–O4	93.70(12)		
Ag (I) center		O4–Cu2–O3	86.33(12)		
Ag1–O1	2.419(3)	O3–Cu2–N3	93.30(13)		
Ag1–O2	2.331(3)	O5–Cu2–N3	82.70(14)		
Ag1–O5	2.413(4)	O5–Cu2–N4	108.88(14)		
Ag1–O6A	2.527(14)	O5–Cu2–O3	96.32(14)		
Ag2–O3	2.356(3)	O5–Cu2–O4	84.59(11)		
Ag2–O4	2.427(3)				
Ag2–O8A	2.491(14)	Cu1–O1–Ag1	104.14(11)		
Ag2–O9A	2.487(14)	Cu1–O2–Ag1	107.62(12)		
		Cu2–O3–Ag2	104.57(12)		
Ag1···Ag2	3.2828(6)	Cu2–O4–Ag2	101.95(11)		

Table 6.9. Structural Parameters (Distances in Å and Angles in º) in the Coordination Environment of Copper(II) and Cadmium(II) Centers in **30**. Symmetries are as in Figures.

Bond lengths		**Bond Angles**			
Cu(II) center		Cu(II) center		Cd (II) center	
Cu1–N1	1.9670(16)	N1–Cu1–O2	161.25(7)	O1–Cd1–O1E	180.0
Cu1–N2	1.9695(16)	N2–Cu1–O1	172.47(6)	O2–Cd1–O2E	180.0
Cu1–O2	1.9382(13)	N1–Cu1–N2	96.10(7)	O4–Cd1–O4E	180.0
Cu1–O1	1.9644(13)	N1–Cu1–O1	90.99(6)	O1–Cd1–O2	69.58(5)
Cu1–O3A	2.420(15)	N2–Cu1–O2	91.73(6)	O1E–Cd1–O2E	69.59(5)
		O1–Cu1–O2	82.27(6)	O1–Cd1–O4	86.92(7)
Cd (II) center		O3A–Cu1–O1	87.4(5)	O1E–Cd1–O4E	86.92(7)
Cd1–O1	2.2566(14)	O3A–Cu1–O2	100.5(4)	O2–Cd1–O4	89.68(6)
Cd1–O2	2.2426(13)	O3A–Cu1–N1	96.6(4)	O2E–Cd1–O4E	89.68(6)
Cd1–O1E	2.2567(14)	O3A–Cu1–N2	89.2(4)	O2–Cd1–O4E	90.32(6)
Cd1–O2E	2.2426(13)			O2E–Cd1–O4	90.32(6)
Cd1–O4	2.3682(18)	Cu1–O1–Cd1	100.03(5)	O1–Cd1–O4E	93.08(7)
Cd1–O4E	2.3682(18)	Cu1–O2–Cd1	101.34(5)	O1E–Cd1–O4	93.08(7)
				O2–Cd1–O1E	110.41(5)
Cu1···Cd1	3.2397(3)			O1–Cd1–O2E	110.42(5)

Comparison of the Structures of 25–30 with Related Systems. A few compounds containing both a bivalent 3d metal ion among Cu^{II} and Ni^{II} and the 5f metal ion, $U^{VI}O_2$, have been previously reported from double-compartmental Schiff base ligands (3-methoxy/ethoxy/3-hydroxysalicylaldehyde–diamine; H_2L^{double}) or single-compartmental Schiff base ligands (salicylaldehyde–diamine or 2-hydroxyacetophenone–diamine; H_2L^{single}).[1, 75–81] Most of those compounds which are derived from H_2L^{double} are cocrystals in which the uranium(VI) center is not coordinated with the phenoxo or methoxy/ethoxy/3-hydroxy oxygen atoms of Schiff base ligand,[1,77–79] while all of those compounds which are derived from H_2L^{single} are discrete dinuclear systems in which the uranium(VI) center is coordinated with the two phenoxo oxygen atoms,[75,76] i.e., those are diphenoxo–bridged as are the three compounds **25** and **27** in the present investigation. On the other hand, only one of the compounds derived from H_2L^{double} (the concerned ligand is 3-ethoxysalicylaldehyde–1,3-diaminopropane, H_2L^{OEt-pn}; Table 6.10) is discrete dinuclear systems in which also the uranium(VI) center is coordinated with the two phenoxo oxygen atoms (i.e., that is also diphenoxo-bridged) but is not coordinated with the ethoxy oxygen atoms as in compound **27** where the copper(II) and uranyl center is

diphenoxobridged. For all of those few diphenoxo-bridged discrete dinuclear 3d–uranyl(VI) compounds, the 3d metal ion is copper(II) and general composition (excluding solvent of crystallization) is $[Cu^{II}(MeCN)L^{single/double}(U^{VI}O_2)(NO_3)_2]$.[75,76,78] Clearly, $[Cu^{II}(acetone)L^5(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$ (**25**), $[Cu^{II}(H_2O)L^7(U^{VI}O_2)(NO_3)_2]\cdot MeCN$ (**26**) and $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**) are among only a few examples of dinuclear 3d–uranyl(VI) compounds and **27** is the only example of discrete dinuclear nickel(II)–uranyl(VI) compound derived from the above mentioned single/double-compartmental Schiff base ligands.[1, 75–81]

An interesting structural aspect is found from the comparison of the structures of the above mentioned diphenoxo-bridged 3d–uranyl(VI) compounds with the available structures of the corresponding mononuclear compounds. The concerned structural aspect is the relative planarity of the two arene rings of a Schiff base ligand in a 3d–uranyl(VI) compound in comparison to the corresponding mononuclear 3d compound. The dihedral angle (δ_{arene}) values between the two arene rings of a Schiff base ligand in the above mentioned Cu^{II}/Ni^{II}–$(U^{VI}O_2)$ compounds as well as in the corresponding mononuclear copper(II) compounds (the structure of only concerned mononuclear Ni^{II} compound is not known and our attempts to get its single crystals have not been successful) are listed in Table 6.10. The δ_{arene} values in the Cu^{II}–$(U^{VI}O_2)$ compounds derived from the single-compartmental ligands lie in the range 61.6–88.6°, while the δ_{arene} values in the corresponding mononuclear copper(II) compounds lie in the range 43.5–47.8°. On the other hand, the δ_{arene} values in the Cu^{II}–$(U^{VI}O_2)$ compounds derived from the double-compartmental ligands lie in the range 22.5–35.1°, while the δ_{arene} values in the corresponding mononuclear copper(II) compounds lie in the range 35.0–41.9°. Hence, the two arene rings are less planar in the Cu^{II}–$(U^{VI}O_2)$ compounds than the Cu^{II} compounds by 16.9–43.4° in the case of the single-compartment ligands, while the two arene rings are more planar in the Cu^{II}–$(U^{VI}O_2)$ compounds than the Cu^{II} compounds by 6.8–12.5° in the case of the double-compartment ligands. Thus, although ethoxy moiety does not coordinate to uranium(VI) center, its presence/absence influences the extent of planarity of the Schiff bases in the Cu^{II}–$(U^{VI}O_2)$ compounds in comparison to the mononuclear Cu^{II} compounds and that effect is consistent.

Table 6.10. Comparative dihedral angles between the two phenyl rings in Cu^{II}/Ni^{II}–($U^{VI}O_2$) and corresponding mononuclear Cu^{II}/Ni^{II} compounds derived from single-/double- compartmental ligands.

Ligand type	**Compound (Excluding solvent)**	**δ_{arene}[b] in M^{II}–U^{VI} (deg)**	**δ_{arene}[b] in Corresponding Mononuclear M^{II} Compound (deg)**	**δ_{arene} (in $M^{II}U^{VI}$) – δ_{arene} (in M^{II}) (deg)**	**Ref.**
Single–compartmental	$[Cu^{II}(acetone)L^{5}(U^{VI}O_2)(NO_3)_2]$ (**25**)	85.0	45.8	39.2	This work
	$[Ni^{II}L^{5}(U^{VI}O_2)(NO_3)_2]$ (**27**)	82.1	—		This work
	$[Cu^{II}(MeCN)L^{Sal-pn}(U^{VI}O_2)(NO_3)_2]$[a]	88.6	45.2	43.4	75
	$[Cu^{II}(MeCN)L^{Sal-2Etpn}((U^{VI}O_2)(NO_3)_2]$[a]	68.3	43.5	24.8	75
	$[Cu^{II}(MeCN)L^{Actp-pn}(U^{VI}O_2)(NO_3)_2]$[a]	81.8	47.8	34	75
	$[Cu^{II}(MeCN)L^{Sal-bn}(U^{VI}O_2)(NO_3)_2]$[a]	61.6	44.7	16.9	76
Double–compartmental	$[Cu^{II}(H_2O)L^{7}(U^{VI}O_2)(NO_3)_2]$ (**26**)	22.5	35.0	–12.5	This work
	$[Cu^{II}(MeCN)L^{Oet-pn}(U^{VI}O_2)(NO_3)_2]$[a]	35.1	41.9	–6.8	78

[a] H_2L^{Sal-pn} = Salicylaldehyde–1,3-diaminopropane; $H_2L^{sal-2Etpn}$ = Salicylaldehyde–2-ethyl-1,3-diaminopropane; $H_2L^{Actp-Pn}$ = 2-hydroxyacetophenone–1,3-diaminopropane; H_2L^{Sal-bn} = Salicylaldehyde–1,4-diaminobutane; H_2L^{8} = 3-ethoxysalicylaldehyde–1,3-diaminopropane. [b] δ_{arene} = Dihedral angle between two arene rings in a Schiff base ligand.

3d–silver(I) compound derived from the above mentioned single-/double-compartmental ligands are only a few. The first example of a 3d–silver(I) compound, which is a trinuclear cocrystal of a diphenoxo-bridged $Cu^{II}Ag^{I}$ and a mononuclear Cu^{II} moiety has been reported from a double-compartmental (3-ethoxysalicylaldehyde–diamine) ligand.[50] Recently, following types of nine copper(II)–silver(I) compounds derived from single-compartmental (salicylaldehyde–diamine or 2-hydroxyacetophenone–diamine; H_2L^{single}) and double-compartment (3-methoxy/ethoxysalicylaldehyde–diamine; H_2L^{double}) Schiff base ligands[47] have been reported: (i) One trinuclear $Cu^{II}Ag^{I}Cu^{II}$ system; (ii) Three dimer-of-dinuclear type $[Cu^{II}Ag^{I}]_2$ systems where $[Cu^{II}L^{single/double}Ag^{I}(NO_3)]$ dinuclear units are interlinked by $Cu^{II}\cdots$O(nitrate) semicoordination and silver(I)$\cdots$silver(I) interaction; (iii) Two dimer-of-dinuclear type $[Cu^{II}Ag^{I}]_2$ systems where $[Cu^{II}L^{double}Ag^{I}(NO_3)]$ dinuclear units are interlinked by Ag^{I}–C (arene; η^1) bond; (iv) One dimer-of-dinuclear type $[Cu^{II}Ag^{I}]_2$ systems where $[Cu^{II}L^{double}Ag^{I}(NO_3)]$ dinuclear units are interlinked by Ag^{I}–C (arene; η^2) bond; (v) One one-dimensional coordination polymer where dinuclear $Cu^{II}Ag^{I}$ units are interlinked by Ag^{I}–C (arene; η^2) bonds; (vi) One one-dimensional coordination polymer where dinuclear $Cu^{II}Ag^{I}$ units are interlinked by Ag^{I}–C (arene; both η^2 and η^3) bonds. Hence, the two copper(II)–silver(I) compounds $[\{Cu^{II}L^{5}Ag^{I}(NO_3)\}_2]$ (**28**) and $[\{Cu^{II}L^{6}Ag^{I}(NO_3)\}_2]$ (**29**) are among only a few 3d–silver(I) compounds derived from Schiff base ligands.[1,47,50] As already discussed, both **28** and **29** are dimer-of-dinuclear compounds. The interactions to form dimer in **29** are $Cu^{II}\cdots$O(nitrate) semicoordination and silver(I)$\cdots$silver(I) interaction, while those are Ag^{I}–C (arene; η^2) bond and silver(I)$\cdots$silver(I) interaction in **28**. Clearly, simultaneous effect of Ag^{I}–C bond and silver(I)$\cdots$silver(I) interaction are new combinations of interactions to form a dimer-of-dinuclear $[Cu^{II}Ag^{I}]_2$ system (**28**).

Compound **30** is a rare example of discrete trinuclear $Cu^{II}Cd^{II}Cu^{II}$ system because just a few such discrete trinuclear compounds from single compartmental Schiff base ligands are known.[1,31,48] However, none of those few previous examples contain perchlorate as a ligand/bridging ligand/anion. Hence, compound **30** which has two bridging perchlorate ligands, each of which bridges a pair of copper(II) and cadmium(II)

centers, is a new type of trinuclear $Cu^{II}Cd^{II}Cu^{II}$ system derived from a single-compartmental Schiff base ligand. It is also worth mentioning that few 3d–cadmium(II) compounds that have been reported from double-compartmental ligands are either cocrystals of dinuclear and mononuclear units or discrete dinuclear systems.[10,50]

Types of previous systems (total: 11) from single-compartmental ligands where the diamine counterpart is 2,2-dimethyl-1,3-diaminopropane: Two dinuclear $Cu^{II}Zn^{II}$; One trinuclear $Cu^{II}Mn^{II}Cu^{II}$; One trinuclear $Cu^{II}Cd^{II}Cu^{II}$;[31] One dimer-of-dinuclear $(Cu^{II}Cu^{II})_2$ (linker is acetate) ;[22] Two dinuclear $Ni^{II}Zn^{II}$;[46] One dinuclear $Ni^{II}Co^{II}$;[28] One trinuclear $Ni^{II}Cu^{II}Ni^{II}$; One trinuclear $Ni^{II}Co^{II}Ni^{II}$; One trinuclear $Ni^{II}Mn^{II}Ni^{II}$.[23] Types of previous systems (total: 35) from double-compartment 3-methoxysalicylaldehyde–diamine ligands where the diamine counterpart is 2,2-dimethyl-1,3-diaminopropane: One trinuclear $Ni^{II}Na^{I}Ni^{II}$;[7] One trinuclear $Cu^{II}Ca^{II}Cu^{II}$ based polymer (linker is nitrate);[8] Two dinuclear $Ni^{II}Y^{III}$;[40,41] One dinuclear $Ni^{II}Y^{III}$ based polymer (linker is octacyanotungstate(V);[1] One dinuclear $Ni^{II}La^{III}$ based polymer (linker is octacyanotungstate(V);[1] Four dinuclear $Cu^{II}Gd^{III}$;[57,60,64,65] Five dinuclear $Cu^{II}Tb^{III}$;[57,58,63,66] Two dinuclear $Cu^{II}Dy^{III}$;[57,58] Two dinuclear $Cu^{II}Ho^{III}$;[57,58] Two dinuclear $Cu^{II}Er^{III}$;[57,58] Two dinuclear $Ni^{II}Gd^{III}$;[40,61] Three dinuclear $Ni^{II}Tb^{III}$;[40] One dinuclear $Ni^{II}Dy^{III}$;[40] One dinuclear $Ni^{II}Ho^{III}$; [40] One dinuclear $Ni^{II}Er^{III}$;[40] One dinuclear $Ni^{II}Yb^{III}$;[67] One trinuclear $Ni^{II}Eu^{III}Ni^{II}$;[69] One trinuclear $Ni^{II}Gd^{III}Ni^{II}$;[68] One dimer-of-dinuclear $(Ni^{II}Gd^{III})_2$ (linker is octacyanotungstate(V);[70] One dimer-of-dinuclear $(Ni^{II}Tb^{III})_2$ (linker is octacyanotungstate(V);[70] One dimer-of-dinuclear $(Ni^{II}Dy^{III})_2$ (linker is octacyanotungstate(V).[70] Types of previous systems (total: 1) from double-compartment 3-ethoxysalicylaldehyde–diamine ligands where the diamine counterpart is 2,2-dimethyl-1,3-diaminopropane One dinuclear $Cu^{II}Gd^{III}$.[74] Clearly, the six compounds **25**–**30**, in this manuscript are among a few examples (in addition to previous 47) of copper(II)/nickel(II)–second metal ion compounds (where the second metal ion is not a lanthanide) derived from single-/double-compartmental Schiff base ligands where the diamine counterpart is 2,2-dimethyl-1,3-diaminopropane.

6.3.2. Diffuse Reflectance Spectra

Diffuse reflectance spectra of **25**–**30** and the corresponding four mononuclear copper(II)/nickel(II) complexes have been measured. The spectra are shown in the following figures: Figure 6.8– $[Cu^{II}L^5]\cdot MeOH$ (**24**), $[Cu^{II}(acetone)L^5(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$ (**25**) and $[\{Cu^{II}L^5Ag^{I}(NO_3)\}_2]$ (**28**); Figure 6.9– $[Ni^{II}L^5]$ and $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**) Figure 6.10– $[Cu^{II}L^6]$, $[\{Cu^{II}L^6Ag^{I}(NO_3)\}_2]$ (**29**) and $[(Cu^{II}L^6)_2Cd^{II}(ClO_4)_2]$ (**30**); Figure. 6.11.– $[Cu^{II}L^7\supset(H_2O)]$ and $[Cu^{II}(H_2O)L^7(U^{VI}O_2)(NO_3)_2]\cdot MeCN$ (**26**);. All the ten compounds show two peaks/shoulders. The λ_{max} values of the two absorptions are listed in Table 6.11. The lower energy absorption arises due to d–d transition, while the higher energy absorption arises due to intraligand transition. For the copper(II) complexes, the range of the d–d transition is 585–650 nm, while characteristic d–d transition for square planar nickel(II) systems appear at 486 nm and 532 nm (shoulder) for $[Ni^{II}L^5]$ and $[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**), respectively (Figure 6.9). On the other hand, the range of the absorption position of intraligand transition in these complexes is 362–400 nm.

A correlation was reported[92] and has been explored recently[75,77,78] regarding the position of d–d transition (λ_{max}) as the function of the displacement (d_{Cu}) of copper(II) ion from the corresponding basal plane. According to this correlation, the d–d band of copper(II) should be blue shifted as d_{Cu} becomes smaller and will be red shifted as d_{Cu} becomes larger. The displacement (d_{Cu}) values of copper(II) from the corresponding basal plane are also listed in Table 6.11. We have reported previously that spectral shift of [copper(II)–diamagnetic metal ion] complexes in comparison to the mononuclear copper(II) complex from a particular ligand follow in some cases the difference of d_{Cu} values of the former complexes and mononuclear complex.[75,77,78] As listed in Table 6.11, d_{Cu} value in **25** is greater by 0.056 in comparison to that in $[Cu^{II}L^5]\cdot MeOH$, while d_{Cu} value in **28** is smaller by 0.024 in comparison to that in $[Cu^{II}L^5]\cdot MeOH$. Along the same line, λ_{max}(d-d) of **25** is greater by 31 nm and that of **28** is smaller by 29 nm in comparison to the mononuclear complex. However, spectra of $[Cu^{II}L^6]$, **29** and **30** as well as spectra

of $[Cu^{II}L^{7}\supset(H_2O)]$ and **26** don't follow the correlation. Clearly, the correlation is not straightforward.

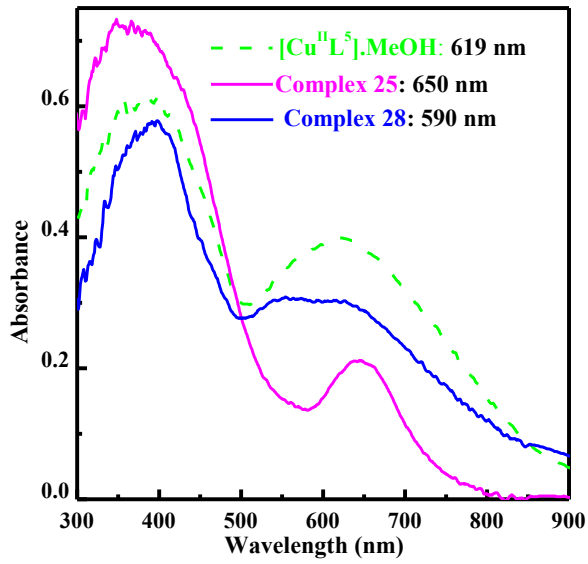

Figure 6.8. Diffuse reflectance spectra, in the range 300–900 nm, of $[Cu^{II}(acetone)L^{5}(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$ (**25**), $[\{Cu^{II}L^{5}Ag^{I}(NO_3)\}_2]$ (**28**) and the corresponding mononuclear copper(II) compound, $[Cu^{II}L^{5}]\cdot MeOH$.

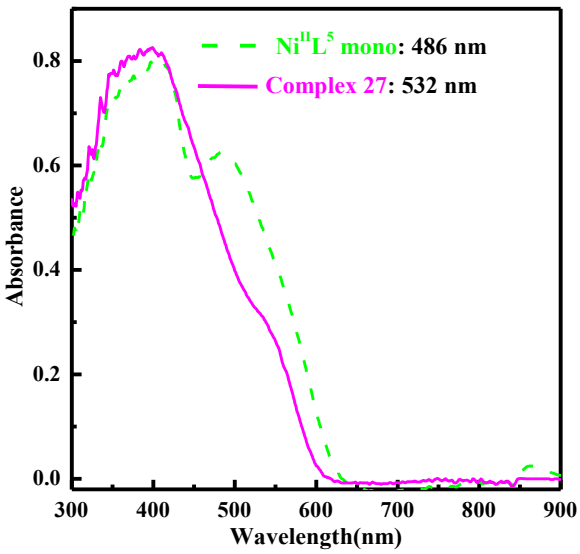

Figure. 6.9. Diffuse reflectance spectra, in the range 300–900 nm, of $[Ni^{II}L^{5}(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**) and the corresponding mononuclear nickel(II) compound $[Ni^{II}L^{5}]$.

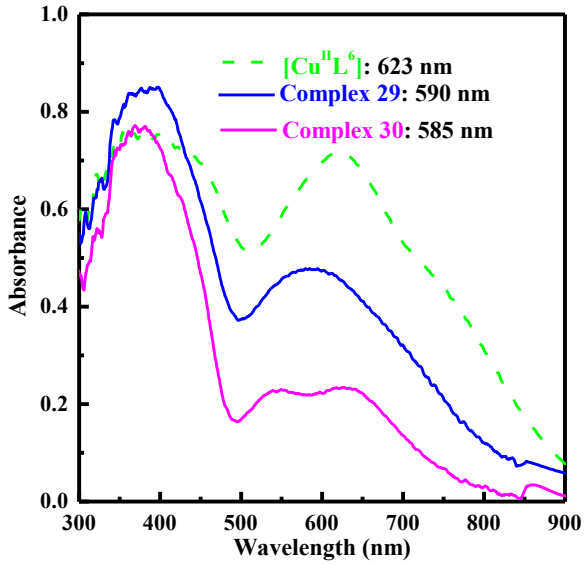

Fig. 6.10. Diffuse reflectance spectra, in the range 300–900 nm, of $[\{Cu^{II}L^{6}Ag^{I}(NO_3)\}_2]$ (**29**) and $[(Cu^{II}L^{6})_2Cd^{II}(ClO_4)_2]$ (**30**) the corresponding mononuclear copper(II) compound $[Cu^{II}L^{6}]$.

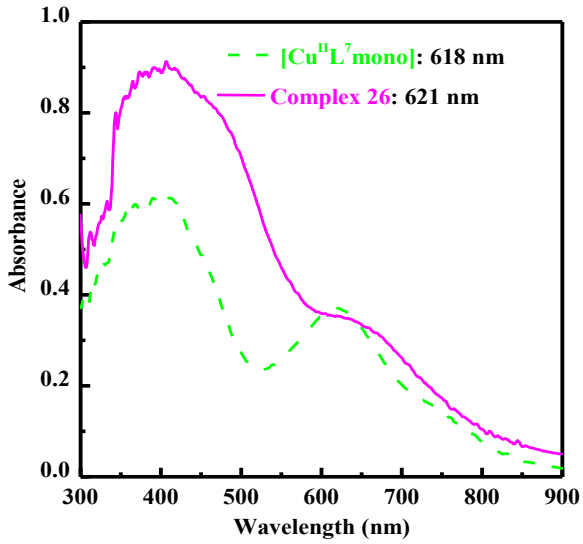

Figure. 6.11. Diffuse reflectance spectra, in the range 300–900nm, of $[Cu^{II}(H_2O)L^7(U^{VI}O_2)(NO_3)_2]\cdot MeCN$ (**26**) and the corresponding mononuclear copper(II) compound $[Cu^{II}L^7\supset(H_2O)]$.

Table 6.11. Spectral parameters and displacement of copper(II)/nickel(II) center from basal plane in mononuclear Cu^{II}/Ni^{II} compounds and compounds **25**–**30**.

	$\lambda_{d\text{-}d}$ (nm)	λ_{ligand} (nm)	$[\lambda_{(heterometallic)} - \lambda_{(Cu^{II}/Ni^{II})}]$(nm)	d_{Cu}(Å)	$[d_{Cu\ (heterometallic)} - d_{Cu(Cu^{II})}]$(Å)
$[Cu^{II}L^5]\cdot MeOH$	619	378	—	0.076	—
$[Cu^{II}(acetone)L^5(U^{VI}O_2)(NO_3)_2]\cdot 1.5CH_3COCH_3$ (**25**)	650	362	31	0.132	0.056
$[\{Cu^{II}L^5Ag^{I}(NO_3)\}_2]$ (**28**)	590 (broad)	393	–29	0.052	–0.024
$[Cu^{II}L^6]$	623	388	—	0.011	—
$[\{Cu^{II}L^6Ag^{I}(NO_3)\}_2]$ (**29**)	590	382	–33	0.076 0.105	0.065 0.094
$[(Cu^{II}L^6)_2Cd^{II}(ClO_4)_2]$ (**30**)	585 (broad)	373	–38	0.115	0.104
$[Cu^{II}L^7\supset(H_2O)]$	618	400	—	0.024	—
$[Cu^{II}(H_2O)L^7(U^{VI}O_2)-(NO_3)_2]\cdot MeCN$ (**26**)	621	398	3	0.215	0.191
$[Ni^{II}L^5]$	486	395	—	—	—
$[Ni^{II}L^5(U^{VI}O_2)(NO_3)_2]\cdot CH_3COCH_3$ (**27**)	532	386	46	—	—

6.4. Conclusions

Heterometallic copper(II)/nickel(II) systems derived from single-/double-compartmental acyclic Schiff base ligands have been further explored in this investigation. Two new mononuclear copper(II)/nickel(II) and six new heterometallic of the following types are reported: Two diphenoxo-bridged Cu^{II}–($U^{VI}O_2$) (**25** and **26**), one diphenoxo-bridged Ni^{II}–($U^{VI}O_2$) (**27**), one dimer-of-dinuclear $[Cu^{II}Ag^{I}]_2$ (**28**) where two diphenoxo-bridged $Cu^{II}Ag^{I}$ units are interlinked by Ag^{I}–C (arene; η^2-mode) bonds and silver(I)····silver(I) interactions, one dimer-of-dinuclear $[Cu^{II}Ag^{I}]_2$ (**29**) where two diphenoxo-bridged $Cu^{II}Ag^{I}$ units are interlinked by Cu^{II}···O(nitrate) semicoordination and silver(I)···silver(I) interaction and one trinuclear linear $Cu^{II}Cd^{II}Cu^{II}$ compound (**30**) where copper(II) and cadmium(II) in each of the two $Cu^{II}Cd^{II}$ pairs are bridged by two phenoxo oxygen atoms and two oxygen atoms of a perchlorate ligand. Major outcomes may be summarized as: (i) Compounds **25**–**27** are among only a few 3d–uranyl compounds from single-/double-compartmental Schiff base ligands;[1,75–81] (ii) Compound **27** is the sole example of dinuclear Ni^{II}–($U^{VI}O_2$) system from single-/double-compartmental Schiff base ligands;[1] (iii) Compounds **28** and **29** are among only a few 3d–silver(I) compounds from single-/double-compartment Schiff base ligands;[1,47,50] (iv) Compound **28** is the sole example of a dimer-of-dinuclear $[Cu^{II}Ag^{I}]_2$ system where two diphenoxo-bridged $Cu^{II}Ag^{I}$ units are interlinked by simultaneous effect of Ag^{I}–C bonds and silver(I)····silver(I) interactions;[1] (v) Compound **30** is among just a few example of discrete trinuclear $Cu^{II}Cd^{II}Cu^{II}$ systems from single-/double-compartmental Schiff base ligands;[1,31,48] (vi) Bis(μ–phenoxo)–μ–perchlorate bridging moiety in compound **30** is new in 3d–cadmium(II) systems from single-/double-compartmental Schiff base ligands;[1] (vii) An interesting structural aspect is found in the Cu^{II}–($U^{VI}O_2$) compounds: two phenyl rings in a Cu^{II}–($U^{VI}O_2$) compounds becomes less planar in comparison to those of the corresponding mononuclear copper(II) compound derived from a single-compartmental ligand, while the situation is reversed for the double-compartmental ligands; (viii) The correlation of d-d band position of copper(II) with the displacement of copper(II) from the least-squares basal plane has been checked and it has been found that the correlation is not straightforward.

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