

Two non-linear azide containing heteronuclear complexes: crystal structure and thermal decomposition

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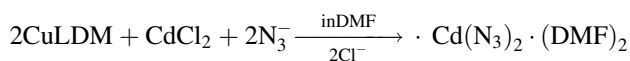
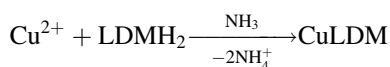
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Abstract Bis-*N,N'*(salicylidene)-2,2'-dimethyl-1,3-propanediamine (LDMH₂) has a high tendency to form polynuclear complexes. Two trinuclear complexes were obtained using this ligand and azide ions; (CuLDM)₂ · Mn(N₃)₂ · (DMF)₂, [(C₁₉H₂₀N₂O₂Cu)₂ · Mn(N₃)₂ · (C₃H₇NO)₂] and (CuLDM)₂ · Cd(N₃)₂ · (DMF)₂, [(C₁₉H₂₀N₂O₂Cu)₂ · Cd(N₃)₂ · (C₃H₇NO)₂]. The structures were identified with X-ray methods. TG and DSC methods were also employed to these complexes. Studies showed the (CuLDM)₂ · Mn(N₃)₂ · (DMF)₂ and (CuLDM)₂ · Cd(N₃)₂ · (DMF)₂ to be non-linear. Also μ -bridges were not encountered for the azide ions but were seen to form between the Cu and other metal via phenolic oxygens. Thermal analysis showed exothermic degradation of the azide ions destroying the trinuclear structure. Although azide containing structures show explosive characteristics, this was not observed for the present compounds.

Keywords Azide containing complexes · Explosives · Molecular structure · TG

Introduction

The tendency of bis-*N,N'*(salicylidene)-1,3-propanediamine (LH₂) and its derivatives to form polynuclear complexes is well known since 1976 [1–14]. Bi- [1, 4, 8], tri [2, 3, 5–7, 9–11], tetra [12] and polynuclear [13] complexes have been reported in literature. LH₂ and its derivatives give mononuclear complexes with Ni(II), Cu(II), Co(II). Ni(II) and Cu(II) ions are coordinated between the two iminic nitrogens and two phenolic oxygens [14]. These mononuclear complexes generally tend to form polynuclear structures through the phenolic oxygens with ions like acetate [15], formate [16], nitrite [17]. Linearity is observed in all these structures. Thus tetra [18] and poly nuclear [19] have been obtained under the same assumption. Azide complexes are generally chain structured. Previously a complex in the form (NiL)₂ · Hg(N₃)₂ was obtained by reaction between NiL and HgCl₂ in azide medium [19]. Similarly CuLDM was prepared from Bis-*N,N'*(salicylidene)-2,2'-dimethyl-1,3-propanediamine, LDMH₂ (C₁₉H₂₂N₂O₂) and reacted with MnCl₂ and CdCl₂ in the presence of azide ions resulting in the formation of two trinuclear complexes.



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In previous studies azide ions were seen to form 1,1 (end-on) μ -bridges [18–20]. In the present study similar μ -bridge structures were expected. The best identification method is X-ray diffraction. IR studies can only give limited information of the formation of μ -bridges [21]. Molecular modelling was done using X-ray methods. As thermal degradation of azide containing complexes show different characteristics like explosive, or simple exothermic reaction [21], TG and DSC studies were also performed. In addition IR studies and metal analysis was also performed.

Experimental

Apparatus

N analysis was performed by the semi micro Kjeldahl method. Metal analysis was done using a GBC Avanta PM model AAS. A few milligram of the complex was dissolved in HNO_3 and 0.5 mL H_2O_2 (30%). This solution was diluted to 100 mL and metal ratios were directly obtained. IR spectrums were obtained on a Mattson FTIR 1000 with KBr disks. Thermal analysis was performed with a Shimadzu DTG-60H and DSC-60 in Ar atmosphere with a heating rate of 10 °C/min between room temperature and 800 °C. In order to assess the organic residue and to determine the metal oxide amount O_2 was purged into the system at this temperature. X-ray data was obtained on a Enraf Nonius CAD-4 diffractometer.

Preparation of complexes

In preparation of the trinuclear complexes firstly mononuclear CuLDM complexes were synthesized.

About 1.55 g (0.005 mole) Bis- N,N' (salicylidene)-2,2'-dimethyl-1,3-propanediamine (LDMH₂) was dissolved in 50 mL EtOH. To this solution 10 mL of dilute NH_3 and the solution of 0.85 g (0.005 mole) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 30 mL hot water was added. The mixture was left to stand for a few hours and the resulting crystals were filtered and dried at 80 °C.

Preparation of $(\text{CuLDM})_2 \cdot \text{Mn}(\text{N}_3)_2 \cdot (\text{DMF})_2$ and $(\text{CuLDM})_2 \cdot \text{Cd}(\text{N}_3)_2 \cdot (\text{DMF})_2$

About 0.372 g (0.001 mole) CuLDM was dissolved in 40 mL of DMF. 0.102 g (0.0005 mole) of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (or 0.133 g $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$) was dissolved in 20 mL hot methanol and the solution of 0.065 g (0.001 mole) NaN_3 in 5 mL hot water was added. The mixture was left to stand for 3–4 days and resulting crystals were filtered and dried in open air.

X-ray structure analysis

For the crystal structure determination, the single-crystal of the compounds **I** and **II** were used for data collection on a Enraf-Nonius CAD4 diffractometer [22] with MoK_α ($\lambda = 0.71073 \text{ \AA}$) radiation using the $\omega/2\theta$ scan mode. The

Table 1 Metal analysis and important IR data of the complexes

Complex	Elemental analysis				Important IR bands/ cm^{-1}							
	Expected/%		Found/%		$\nu_{\text{C-H(Ar)}}$	$\nu_{\text{C-H (Aliph)}}$	ν_{N_3}	$\nu_{\text{C=O DMF}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=C}}$	δ_{CH_2}	$\delta_{\text{C-H(Ar)}}$
	Cu	M	Cu	M								
$(\text{CuLDM})_2 \cdot \text{Mn}(\text{N}_3)_2 \cdot (\text{DMF})_2$	12.36	(Mn) 5.35	12.07	(Mn) 5.41	3024	2866	2047	1648	1632	1596	1474	756
					3051	2935	2076					
$(\text{CuLDM})_2 \cdot \text{Cd}(\text{N}_3)_2 \cdot (\text{DMF})_2$	11.70	(Cd) 10.35	12.47	(Cd) 10.96	3016	2865	2041	1650	1631	1596	1475	754
					3049	2923						

Table 2 Thermoanalytical data of the complexes

Complex	1st thermal reaction			2nd thermal reaction			Metal oxide residue	
	Temperature range/°C	Expected mass loss/%	Mass loss found/%	Temperature range/°C	Expected mass loss/%	Mass loss found/%	Expected/%	Found/%
$(\text{CuLDM})_2 \cdot \text{Mn}(\text{N}_3)_2 \cdot (\text{DMF})_2$	157–358 DTA Peak: 309	26.05	24.54 ± 0.16	360–748	–	21.87 ± 1.12	26.05	25.18 ± 1.14
$(\text{CuLDM})_2 \cdot \text{Cd}(\text{N}_3)_2 \cdot (\text{DMF})_2$	167–354 DTA Peak: 311	24.46	24.28 ± 0.36	360–735	–	37.64 ± 1.02	16.92	17.40 ± 1.24

cell parameters were determined from least-squares analysis using 25 centered reflections in the range $2.18^\circ \leq \theta \leq 21.94$ for compound **I** and $2.24^\circ \leq \theta \leq 25.61$ for compound **II**. Three standard reflections were periodically measured (every 120 min) during data collection and showed no significant intensity variations. The structures were solved by direct methods (SHELXS-97)[23] and non-H atoms were refined by full-matrix least-squares method with anisotropic temperature factors (SHELXL-97) [23] in the WinGX package [24].

Results and discussion

The metal analysis results as well as important IR bands are given in Table 1. In addition to Cu, Mn and Cd analysis, N analysis could not be done as during digestion with H_2SO_4 N_2 is formed leading to error in the N results. Thermal analysis results support elemental analysis results. Table 2 shows the thermoanalytical results of the complexes. Two thermal reactions can be seen. The first is an exothermic

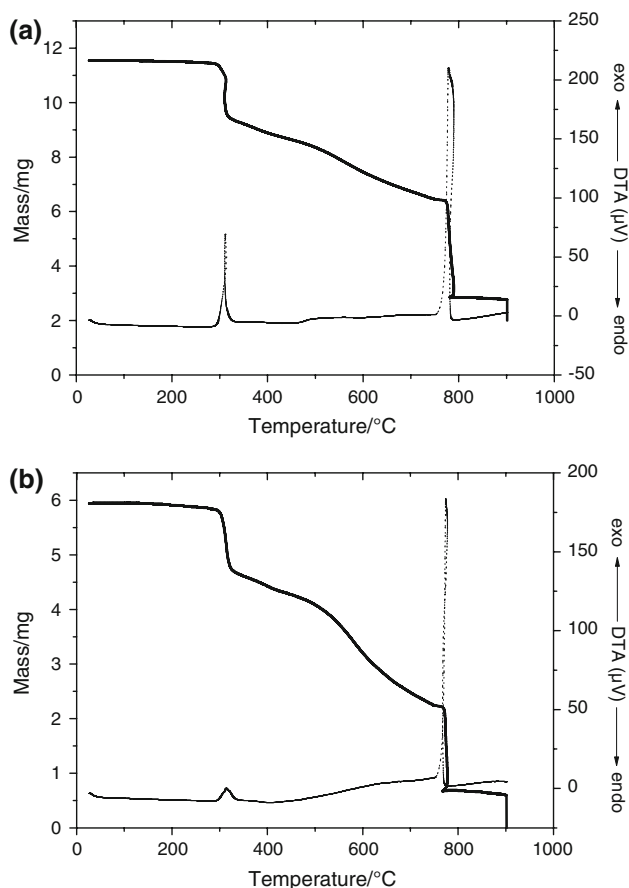


Fig. 1 **a** The TG curve of $(\text{CuLDM})_2 \cdot \text{Mn}(\text{N}_3)_2 \cdot (\text{DMF})_2$. **b** The TG curve of $(\text{CuLDM})_2 \cdot \text{Cd}(\text{N}_3)_2 \cdot (\text{DMF})_2$

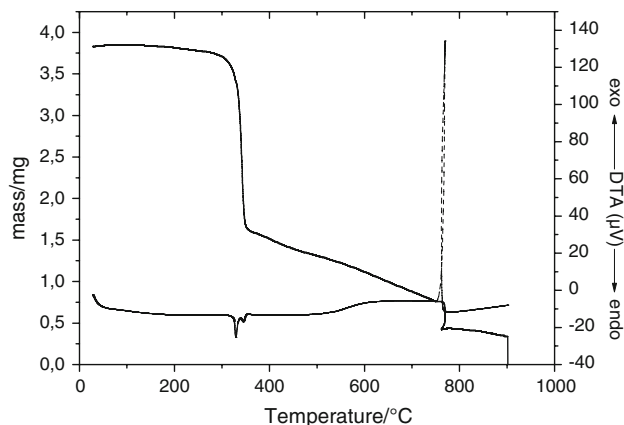


Fig. 2 The TG curve of CuLDM

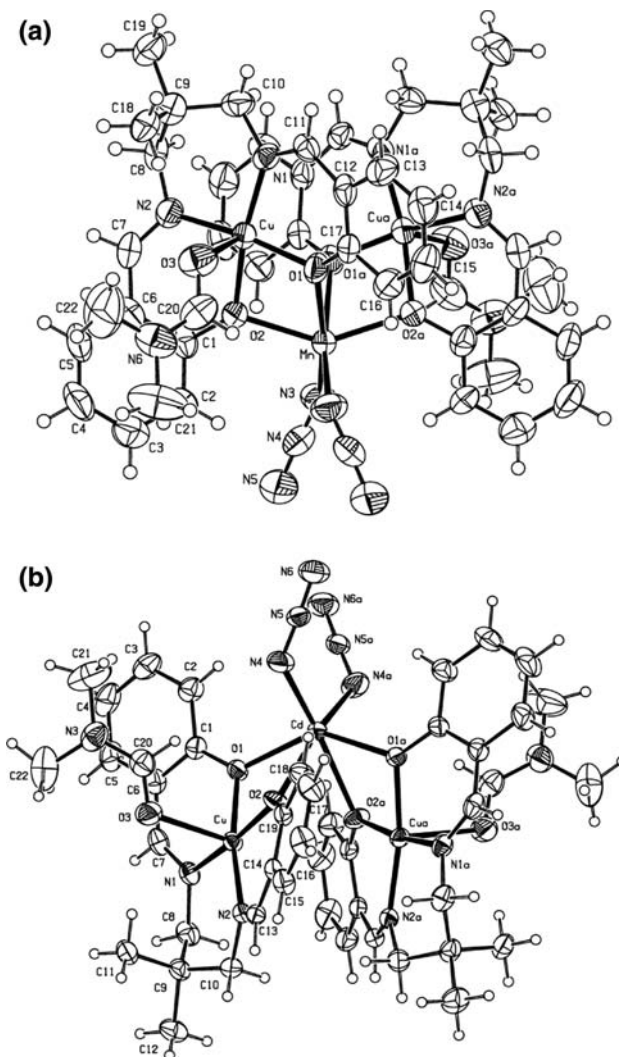


Fig. 3 **a** The Platon drawing of CuMnCu (**I**). **b** The Platon drawing of CuCdCu (**II**)

Table 3 Crystal and experimental data

	I	II
Chemical formula	C ₄₄ H ₅₄ Cu ₂ MnN ₁₂ O ₆	C ₄₄ H ₅₄ Cu ₂ CdN ₁₂ O ₄
CCDC No.	714976	714977
Formula weight	1029.01	1054.47
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, space group	Orthorhombic, P ccn	Orthorhombic, P ccn
Unit cell dimensions: (Å, °)		
a	13.9278(12)	13.8382(12)
b	15.3027(13)	15.3944(11)
c	22.3371(13)	22.5753(13)
Volume (Å ³)	4760.8(6)	4809.2(6)
Z	4	4
Calculated density (g cm ⁻³)	1.436	1.456
Absorption coefficient (mm ⁻¹)	1.206	1.368
F(000)	2132	2160
Crystal size (mm)	0.35 × 0.30 × 0.20	0.28 × 0.24 × 0.20
θ _{max} (°)	43.9	51.2
Index range	0 ≤ h ≤ 14, -16 ≤ k ≤ 0, -23 ≤ l ≤ 12	-16 ≤ h ≤ 0, -18 ≤ k ≤ 0, -26 ≤ l ≤ 0
Number of reflections used	2630 (I ≥ 2σ(I))	4229 (I ≥ 2σ(I))
Number of parameters	294	295
R _{int}	0.016	0.052
R	0.051	0.028
R _w	0.145	0.074
Goodness of fit	1.03	1.14
Δρ _{min} , Δρ _{max} (e Å ⁻³)	-0.59, 0.46	-0.27, 0.27

thermal reaction beginning at 60 °C with a small mass loss increasing between 295–325 °C. The second is a thermal degradation reaction beginning at 330 °C and ending at 750 °C.

The values seen in Table 2 are the mean values at three TG curves. An example is given in Fig. 1a, b. A fast mass loss is between 295–325 °C corresponding to a 25% loss. The mass loss corresponds to the total mass of DMF and azide groups. In the first reaction the mass loss is the result of degradation of azide groups and vapourization of DMF molecules. In previous studies of the coordinative DMF molecules were seen to be endothermic [25, 26], whereas degradation of azide molecules were exothermic. Sometimes thermal degradation of azide molecules were in the form explosions [21]. In their study the exothermic reaction in partially compensated by the endothermic reaction. DSC results show small exothermic heat values for azide reaction; 107.87 ± 8.12 and 315.25 ± 30.49 kJ.mole⁻¹ for (CuLDM)₂ · Cd(N₃)₂ · (DMF)₂ and (CuLDM)₂ · Mn(N₃)₂ · (DMF)₂, respectively. The second reaction corresponds to the thermal degradation of the CuLDM residue. During degradation of azide ions the rest of the complex structure is also altered. TG analysis of

CuLDM shows degradation up to 360 °C (Fig. 2). The present complexes show continuous mass loss between 360 and 730 °C. The mass loss in the Cd containing complex is faster than the Mn containing complex. This is probably due to complete degradation of the complex during azide degradation. Due to carbonization during degradation slower mass loss is observed. During degradation metallic Cd and Mn is obtained. With increasing temperature Cd vaporizes resulting in a higher mass loss. Purging of O₂ to the Cd containing complex after 750 °C resulted in total oxidation of the organic part. The residue is seen to be in the same amount as expected of CuO. In the Mn containing complex the residue is the same amount as the total of CuO + MnO.

The molecular models of the complexes are shown in Fig. 3a, b as Platon drawing [27]. X-ray crystal data have been given in Table 3 and the coordinative bond angles in Table 4. The two terminal Cu(II) ions in both complexes possess a square pyramid (tetragonal) coordination sphere. The bond angles in the vicinity of Cu(II) show the coordination sphere to be almost ideal (Table 4). A τ value has been given in literature for penta component coordination sphere [28].

Table 4 Selected bond angles (°) of the compounds **I** and **II**

I		II	
O1CuO2	80.9 (3)	N4 ⁱ CdN4	102.77 (15)
O1CuN1	92.3 (3)	N4 ⁱ CdO1	104.50 (10)
O2CuN1	170.4 (3)	N4CdO1	100.54 (10)
O1CuN2	170.5 (3)	O1CdO1 ⁱ	139.37 (9)
O2CuN2	90.1 (3)	N4 ⁱ CdO2	163.86 (9)
N1CuN2	96.2 (3)	N4CdO2	92.03 (9)
O1CuO3	90.6 (3)	O1CdO2	65.91 (6)
O2CuO3	91.6 (3)	O1 ⁱ CdO2	81.61 (7)
N1CuO3	95.3 (3)	N4 ⁱ CdO2 ⁱ	92.03 (9)
N2CuO3	92.8 (3)	N4CdO2 ⁱ	163.86 (9)
N3MnN3 ⁱ	98.7 (6)	O2CdO2i	74.12 (10)
N3MnO2	101.9 (3)	O2CuO1	82.08 (7)
N3 ⁱ MnO2	101.0 (3)	O2CuN2	92.06 (8)
O2 ⁱ MnO2	144.5 (3)	O1CuN2	170.15 (8)
N3MnO1	166.1 (3)	O2CuN1	171.73 (8)
N3 ⁱ MnO1	93.4 (3)	O1CuN1	89.74 (8)
O2 ⁱ MnO1	83.0 (2)	N2CuN1	95.89 (9)
O2MnO1	68.9 (2)	O2CuO3	89.34 (9)
N3MnO1 ⁱ	93.4 (3)	O1CuO3	91.67 (8)
N3 ⁱ MnO1 ⁱ	166.1 (3)	N2CuO3	96.19 (8)
O2 ⁱ Mn O1 ⁱ	68.9 (2)	N1CuO3	92.04 (9)
O2MnO1 ⁱ	83.0 (2)	N6N5N4	176.3 (4)
O1MnO1 ⁱ	75.5 (4)	CuO1Cd	103.34 (7)
N3N4N5	176.8 (13)	CuO2Cd	99.54 (8)
CuO1Mn	98.4 (3)		
CuO2Mn	102.1 (3)		

$$\tau = \frac{\alpha - \beta}{60}$$

α and β are the largest two angles around the Cu(II) ion. The τ values for $(\text{CuLDM})_2 \cdot \text{Cd}(\text{N}_3)_2 \cdot (\text{DMF})_2$ and $(\text{CuLDM})_2 \cdot \text{Mn}(\text{N}_3)_2 \cdot (\text{DMF})_2$ are 0.0263 and 0.0026, respectively. If the value is 0 the coordination is said to be an ideal square pyramid, if 1 is an ideal trigonal bipyramid. The values obtained are very close to 0 meaning the Cu(II) coordination sphere is almost ideal. On the other hand the coordination sphere at Mn(II) and Cd(II) is a distorted octahedral. The distortion can be seen from the bond angles in Table 4.

The summit of the pyramid within the Cu(II) coordination sphere is the DMF oxygen (O_3 atom). The bond length between the oxygen and Cu(II) was found as 2.388 and 2.386 Å which was 0.4 Å longer than the other Cu–O bonds. The most interesting chelate ringing these complexes is the membered CuN1C8C9C10N2 ring. The chelate ring is in a chair conformation but due to the iminic sp^2 hybrids the N atoms have been forced from ideal towards

the plane. Cu(II) is 0.299 Å away from the N1C8C10N2 plane and has an angle of 13.12° with the N1CuN2 plane. On the other hand the angle between the C8C9C10 and N1C8C10N2 planes is approximately 60° (59.95 and 45.93) and C9 atom lies 0.7630 Å away from this plane. The C8C9C10 part of the six membered ring is close to the ideal chair well as N2CuN1 part is far from ideal.

Previous studies have shown DMF molecules to vapourize between 160–240 °C [26, 27]. Although a small mass loss is observed between these temperatures, the main mass loss is observed between 295–325 °C. This temperature is where N_3^- ions are degraded. It is a high probability that the coordinated DMF molecules do not leave the complex structure until the degradation of N_3^- ions, because no endothermic reaction is observed. With the degradation of the azide ions DMF molecules also leave the structure, but as degradation of azide ions are highly exothermic only a strong exothermic reaction is observed. Normally one does not expect the coordinated DMF to stay in the structure up to 295 °C. But CuLDM is bonded to the Mn(II) and Cd(II) ions via the phenolic oxygens μ -bridges, transferring some electrons to the metal ions. In this case the electron density from the phenolic oxygen to the Cu(II) ions in CuLDM is decreased. This is compensated by coordination of the solvent molecule via the O1N1N2O2 plane. If the coordinative DMF molecules are lost electrons of the phenolic oxygen may be insufficient for both metal ions. As a result DMF molecules stay in the structure until the specified temperature. With degradation of the azide groups, the complex structure is destroyed and the DMF molecules easily leave the complex structure. Degradation of azide ion is an exothermic reaction mostly explosive. However, weak exothermic reaction observed in these complexes shows that these complexes are not explosive. The residue after 350 °C shows slow mass loss leading to carbonization. Purging of O_2 into the system all of the organic residue is lost leaving only metal oxides.

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References

- Butcher RE, Sinn E. Relation between magnetic, spectroscopic, and structural properties of bis[chloro(N-isopropyl-2-hydroxybenzylidene)aminato- μ -O)copper(II)] and bis(N-isopropyl-2-hydroxybenzylideneaminato)copper(II). *Inorg Chem.* 1976;15:1604–8.
- Fukuhara C, Tsuneyoshi K, Matsumoto N, Kida S, Mikuriya M, Mori M. Synthesis and characterization of trinuclear Schiff-base complexes containing sulphur dioxide or hydrogensulphite ions as bridging groups. Crystal structure of $[\text{Zn}\{\mu\text{-CH}_3\text{CO}_2\}(\text{salpd-}\mu\text{-O,O})\text{Cu}]_2$ [salpd = propane-1,3-diybis(salicylideneimine)]. *J Chem Soc Dalton Trans.* 1990;3473–9.

- Gerli A, Hagen KS, Marzilli LG. Nuclearity and formulation of SALPN₂-complexes formed from M(O₂CCH₃)₂: resolution of longstanding problems by X-ray crystallography. *Inorg Chem.* 1991;30:4673–6.
- Arıcı C, Svoboda I, Sarı M, Atakol O, Fuess H. {Bis(N,N-dimethylformamide)-N,N'-bis(salicylidene)-1,3-propane-diaminato}nickel(II) dibromozinc(II). *Acta Crystallogr Sect C.* 2001;C57:31–2.
- Atakol O, Nazır H, Arıcı C, Durmuş S, Svoboda I, Fuess H. Some new Ni-Zn heterodinuclear complexes: square pyramidal nickel(II) coordination. *Inorg Chim Acta.* 2003;342:295–300.
- Atakol O, Durmuş S, Durmuş Z, Arıcı C, Çiçek B. Investigations, on some heterotrinnuclear complexes of nickel(II) and copper(II). *Synth React Inorg Met Org Chem.* 2001;31:1689–704.
- You ZL, Zhu HL, Liu WS. Solvothermal syntheses and crystal structures of three linear trinuclear Schiff base complexes of zinc(II) and cadmium(II). *Z Anorg Allg Chem.* 2004;630:1617–22.
- Colon ML, Qian SY, Vanderveer D, Bu XR. Chiral bimetallic complexes from chiral salen metal complexes and mercury(II) halides and acetates: the anionic groups interact with Cu(II) in apical position. *Inorg Chim Acta.* 2004;357:83–8.
- Song Y, Gamez P, Roubeau O, Mutikainen I, Turpeinen U, Reedijk J. Structure and magnetism of two new linear trinuclear copper(II) clusters obtained from the tetradentate N₂O₂ ligand bis(2-hydroxybenzyl)-1,3-diaminopropane. *Inorg Chim Acta.* 2005;358:109–15.
- Reglinski J, Taylor MK, Kennedy AR. Hydrogenated Schiff base ligands: towards the controlled organisation of open metal frameworks. *Inorg Chem Commun.* 2006;9:736–9.
- Shi DH, You ZL, Xu C, Zhang Q, Zhu HL. Synthesis, crystal structure and urease inhibitory activities of Schiff base metal complexes. *Inorg Chem Commun.* 2007;10:404–6.
- Mikuriya M, Ikenoue S, Nukada R, Lim JW. Synthesis and structural characterization of tetranuclear zinc(II) complexes with a linear array. *Bull Chem Soc Jpn.* 2001;74:101–2.
- Mikuriya M, Tsuru N, Ikemi S, Ikenoue S. High nuclearity in a zinc(II) complex with 1,3-bis(salicylamino)-2-propanol. *Chem Lett* 1998;879–80.
- Drew MGB, Prasad RN, Sharma RP. Structures of (N,N'-Trimethylenedisalicylideneaminato) Nickel(II) (1) and (N,N'-Trimethylenedisalicylideneaminato) Copper(II) (2). *Acta Crystallogr Sect C.* 1985;C41:1755–8.
- Ercan F, Ülkü D, Atakol O, Dinçer FN. Bis-acetato-bis-salicylidene-1,3-propandiaminatocopper(II)cadmium(II)-dioxane solvate. *Acta Crystallogr Sect C.* 1998;C54:1787–90.
- Arıcı C, Ülkü D, Atakol O. Crystal structure of bis((N,N'-dimethylformamide)(muformato)(mu-bis(salicylidene)1,3-propanediaminato)nickel(II)cobalt(II)monohydrate. *Anal Sci.* 2002;18:959–60.
- Ercan F, Atakol O, Arıcı C, Svoboda I, Fuess H. Three nuclear Schiff base complexes of nickel(II) with cobalt(II), copper(II) and manganese(II). *Acta Crystallogr Sect C.* 2002;C58:m193–6.
- Koner S, Saha S, Okamata K, Tuchagues JP. A novel tetranuclear copper(II) complex with alternating μ 1,1-azido and phenoxo bridges: synthesis, structure, and magnetic properties of [Cu₄(μ -salen)₂(μ 1,1-N₃)₂(N₃)₂]. *Inorg Chem.* 2003;42:4668–72.
- Reddy KR, Rajasekharan MV, Tuchagues JP. Synthesis, structure, and magnetic properties of Mn(salpn)N₃, a helical polymer, and Fe(salpn)N₃, a ferromagnetically coupled dimer (salpnH₂ = N,N'-bis(salicylidene)-1,3-diaminopropane). *Inorg Chem.* 1998;37:5978–82.
- Tatar L, Ülkü D, Atakol O, Kurtaran R. Crystal structure of a tetramer zinc complex. *Anal Sci.* 2002;18:1171–2.
- Dinçer Kaya FN, Svoboda I, Atakol O, Ergun Ü, Kenar A, Sarı M, et al. Nickel(II) complexes prepared from NNN type ligands and pseudohalogens—synthesis, structure and thermal decomposition. *J Therm Anal Calorim.* 2008;92:617–24.
- Enraf Nonius: Cad-4 Express Version 1.1. Delft, The Netherlands, 1993.
- Sheldrick GM. SHELXS97 and SHEXL97. Program for crystal structure solution and refinement. Germany: University of Göttingen; 1997.
- Farrugia LJ, Win GX. Program for crystallography package. *J Appl Cryst.* 1999;32:837.
- Durmuş S, Ergun Ü, Jaud JC, Emregül KC, Fuess H, Atakol O. Thermal decomposition of some linear trinuclear Schiff base complexes with acetate bridge. *J Therm Anal Calorim.* 2006;86:337–46.
- Ateş BM, Ercan F, Aksu ML, Atakol O. Crystal structure of a new homo trinuclear Ni(II) complex with mu-cyanoacetato bridge. *Z Kristallogr.* 2008;223:530–5.
- Spek AL. PLATON. Program for crystal molecular drawing. The Netherlands: University of Utrecht; 2000.
- Addison AW, Rao TN, Reedijk J, Van Rijn J, Verschoor GC. Synthesis, structure, and spectroscopic properties of copper(II) compounds containing nitrogen-sulphur donor ligands; the crystal and molecular structure of aqua[1,7-bis(N-methylbenzimidazol-2-yl)-2,6-dithiaheptane]copper(II) perchlorate. *J Chem Soc Dalton Trans* 1984;1349–56.