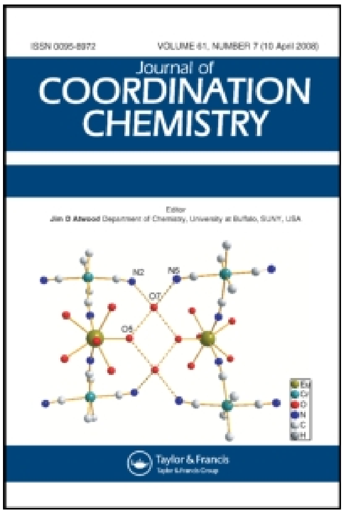

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Self-assembling tetranuclear complexes of a tridentate Schiff base

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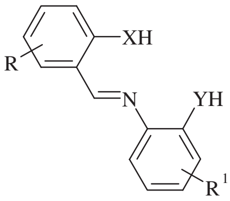
A tetranuclear KZn_3 complex consisting of three tridentate dibasic N_2O donor ligands (derived from mono-N-phenyl-substituted 5-nitro-*o*-phenylenediamine) and one methylato group has been synthesized. Single-crystal multi-temperature (100–350 K) X-ray diffraction studies of the complex reveal that $\{[ZnL]_3OMe\}^-$ units are assembled by K … ON_2 contacts into layers. Mutual position of the KO_6 and $\{[ZnL]_3OMe\}^-$ fragments of neighboring layers is temperature dependent.

Keywords: Schiff base; Tetranuclear metallochelates; Self-assembled crystal structure

1. Introduction

Pronounced interest has been focused on the synthesis and properties of coordination compounds of tridentate dibasic Schiff bases (**1**) with proton donating group positions convenient for formation of mono- (**2**) or dinuclear (**3**) complexes [1–7].



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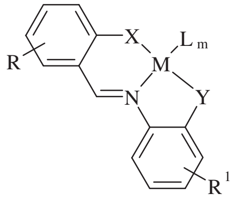

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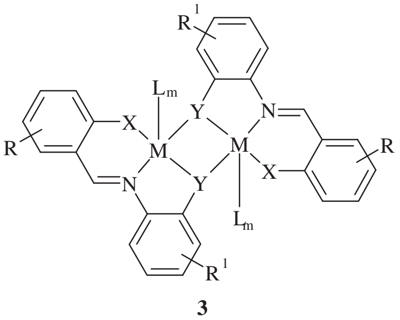

3

X, Y = NR^2, O, S; R, R^1 = H, Hal, NO_2; R^2 = Ar, Ts; L = MeOH, Py, Phen, 1-Me-2-NH_2Bzm; m = 0-2

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In the present paper we report unusual coordination behavior of an azomethine derived from salicylaldehyde and 2-phenylamino-5-nitroaniline by the reaction with zinc acetate in the presence of potassium hydroxide.

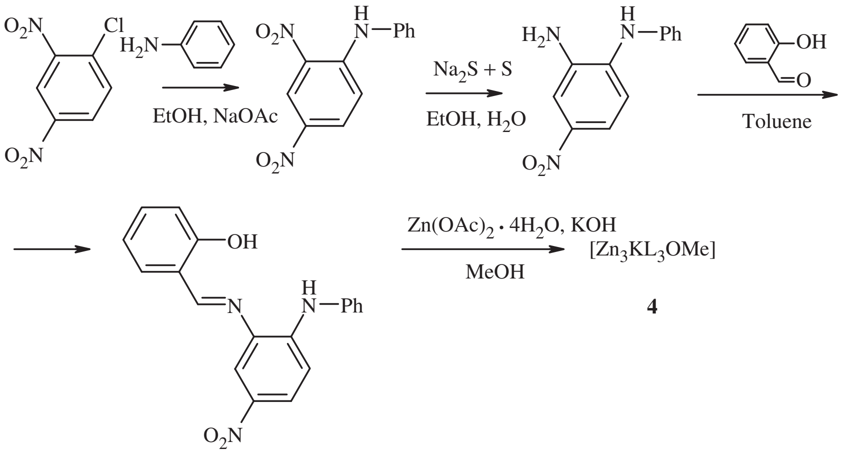
2. Experimental

2.1. *Synthesis*

The synthetic procedure of ligand and its complex is represented in scheme 1.

2.1.1. Ligand 1 (X = O, Y = NPh, *R* = H, R^1 = 5-NO_2). 2-Salicylideneamino-4-nitro-N-phenylaniline was synthesized by refluxing 0.23 g (1 mmol) of 2-phenylamino-5-nitroaniline [8] and 0.12 g (1 mmol) of 2-hydroxybenzaldehyde in 10 mL of toluene with a Dean-Stark trap for 2 h. After evaporation of 2/3 of total solvent volume, ethanol (10 mL) was added. The resulting mixture was cooled to Room temperature and the precipitate was filtered off and crystallized from toluene/ethanol (1 : 2 v/v). Yield 80%. Yellow crystals, m. p. 195°C. *Anal.* Found: C, 68.48; H, 4.58; N 12.51%. Calcd for $C_{19}H_{15}N_3O_3$: C, 68.46; H, 4.54; N, 12.61. ^{1}H NMR (300 MHz, δ ppm, from TMS in $CDCl_3$): 6.20 (s, 1H, NH), 6.85–7.46 (m, 13H, H_{arom}), 8.64 (s, 1H, HC=N), 12.83 (s, 1H, OH).

2.1.2. Complex 4. Complex **4** was obtained by refluxing of 0.33 g (1 mmol) of the ligand and 0.219 g (1 mmol) of zinc acetate dihydrate in methanol (50 mL) for 10 h. After cooling to room temperature, 10 mL of methanol solution of 0.11 g of KOH was added. Red-brown crystals formed and were filtered off, washed with methanol and dried at 120°C. Yield 60%. M. p. > 300°C. Found: C, 55.38; H, 3.38; N 10.12%. Calcd for



Scheme 1. Synthetic procedures for the ligand (**1**) and its complex (**4**).

$C_{57}H_{39}N_9O_9Zn_3.KOCH_3$: C, 55.28; H, 3.36; N, 10.00. The substance decomposes in all deuterosolvents available.

2.2. *Physical measurements*

Elemental analyses (C, H and N) were performed on a Carlo Erba Instruments TCM 480 analyzer. NMR ^{1}H spectrum was recorded on a Varian UNITY-300 spectrometer.

2.3. *X-ray crystallographic analysis and data collection*

X-Ray diffraction experiments were carried out using graphite monochromated Mo-Kα radiation with a Bruker SMART APEX II CCD area detector (ω-scans) at 100, 150 and 200 K, with Nonius CAD 4 ($\theta/2\theta$ -scans) at 298 K and with Bruker SMART 1000 CCD (ω-scans) at 360 K. The structure was solved by direct methods and refined by the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms.

Analysis of the difference Fourier map revealed that in **4** the potassium cation is disordered in two positions, which are located at the three-fold axis. In addition to potassium the phenyl ring (C(14)-C(19) atoms) is also disordered over two positions (the C(17) atom for two positions coincides). It should be noted that for two positions of phenyl ring the values of occupancies 0.6 and 0.4 are unchanged with temperature, while for potassium the disorder is clearly dynamic in nature. As it can be seen from the corresponding table 1 the occupancy factor for K(1) (major position) decreases in a linear fashion with temperature down to 0.803 at 360 K. Refinement of potassium positions in **4** was carried with **SUMP** instruction to constrain the total occupancy to one. For K(1) the thermal motion parameters were described in anisotropic approximation, while for K(1') isotropic description was used. The positions of hydrogen atoms in **4** were calculated.

Crystal data and structure refinement parameters for **4** are given in table 1. All calculations were performed using the SHELXTL software [9]. Crystallographic data (excluding structure factors) for the structures reported have been deposited at the Cambridge Crystallographic Data Centre as supplementary no. CCDC 649543–649547 (see table 1). Copies of the data can be obtained free of charge via www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ UK; fax: +44-1223-336-033; or deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. *Synthesis*

Tridentate dibasic Schiff bases of type (**1**) usually form mono- (**2**) or dinuclear (**3**) complexes [1–7].

However, we have found that the interaction of **1** (X = O, Y = NPh, R = H, R^1 = 5-NO_2) with zinc acetate in methanol in the presence of KOH affords the tetranuclear $[Zn_3KL_3OMe]$ complex **4** (where L is twice deprotonated ligand) instead of the expected complexes **2** or **3** (scheme 2).

Table 1. Summary of crystallographic data and experimental details for **4**.

	4				
Empirical formula	$C_{58}H_{40}KN_9O10Zn_3$				
Formula weight	1258.20				
F(000)					
Crystal system	Monoclinic				
Space group	*R*–3				
Z(*Z*′)	6(0.33)				
Temperature (K)	100(2)	150(2)	200(2)	298(2)	360(2)
	649543	649544	649545	649546	649547
a (Å)	19.5770(8)	19.576(1)	19.577(1)	19.560(3)	19.525(5)
c (Å)	23.185(1)	23.338(1)	23.473(1)	23.778(5)	23.979(9)
V (Å^3)	7695.5(8)	7745.4(7)	7791.5(7)	7878(2)	7917(4)
s.o.f. K(1)	**0.959**	**0.932**	**0.899**	**0.840**	**0.803**
D_{calc} (g cm^{-1})	1.629	1.618	1.609	1.591	1.583
Linear absorption, μ (cm^{-1})	15.46	15.36	15.27	15.10	15.02
2θ max (°)	70	58	58	62	58
Reflections measured	76753	13007	6955	6737	22183
Independent reflections	7510	4224	4259	6054	4559
Observed reflections [$I > 2\sigma(I)$]	6297	3351	3129	3828	3012
Final $R(F_{\mathrm{hkl}})$: R_1	0.0422	0.0377	0.0424	0.0659	0.0522
wR_2	0.1167	0.0996	0.1110	0.1798	0.1377
GOF	1.032	1.024	1.035	1.030	0.928
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	1.5, −1.38	0.61, −0.85	0.84; −0.78	1.25; −0.93	0.95; −0.90

X-ray diffraction studies of **4** reveal that the crystal consists of the $\{[ZnL]_3OMe\}^-$ species connected by potassium atoms. Triangular-pyramidal N_2O_3 coordination environment of each zinc ion is built by two phenolato and one methylato oxygen atoms, one amine and one azomethine nitrogen atoms (figure 1). The Zn...Zn separations in the anion is 3.1093(3)Å.

The potassium ions are disordered over two positions (see experimental section), each playing a different role in the crystal of **4**. The major potassium position (with maximum population) K(1) forms the Zn_3KO_4 pseudo-cube structure (figure 1) and is coordinated by three oxygens corresponding to phenolato moieties and by three oxygens of NO_2 groups (K(1)...O(2) 2.645(1)Å at 100–360 K) of neighboring anions. The Zn...K(1) separation is equal to 3.9523(8) at 100K and 4.022(2)Å at 360K.

In contrast, the K(1') with minor occupancy is coordinated solely by NO_2 groups (K...O 2.743(4)- 2.799(8) at 100 K and 2.728(4)–2.767(4)Å at 360K) of three $\{[ZnL]_3OMe\}^-$ species (figure 2).

Analysis of crystal packing clearly shows that both potassium atoms assemble anions into layers parallel to the crystallographic plane *ab*. (figure 3) Thus as shown in figure 2, potassium cation can move in the small cavity between two bulky anions. The walls of this cavity are formed by NO_2 groups of neighbor anions with the longest dimension directed along the crystallographic axis *c*. Taking into account the fact that only unit cell parameter *c* increases with temperature from 23.185(1) at 100 K up to 23.979(9)Å at 350 K (unit cell parameter a is slightly decreased) we can expect the dynamic disorder observed to result from concurrence of K...O_2N and K...O_3Zn interactions. Further studies of disorder in potassium crystal as a function of temperature (including DSC experiments and MD simulations) will help us to rationalize the results obtained.

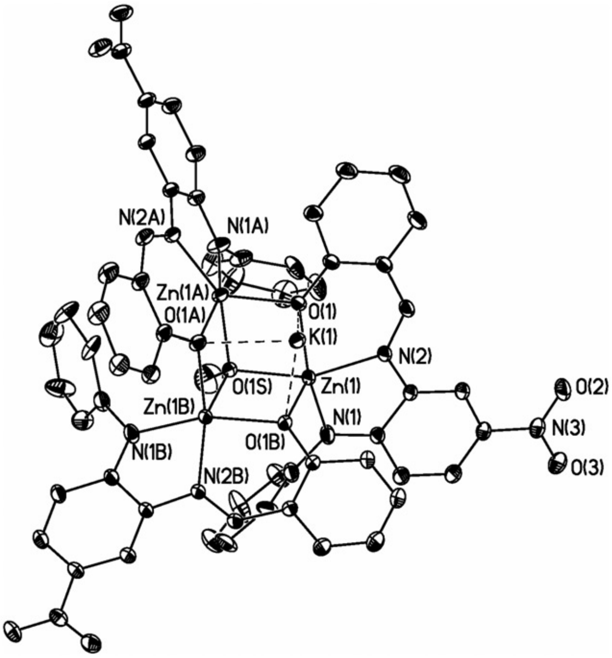


Figure 1. Structure of Zn_3KO_4 coordination unit with thermal ellipsoids ($p = 50\%$). The disordered phenyl rings are removed for clarity. Atoms denoted by labels containing A and B are obtained from the base structure by symmetry operations. Selected bond lengths at 100 K (Å): Zn(1)–N(1) 2.010(1), Zn(1)–O(1B) 2.053(1), Zn(1)–O(1S) 2.057(1), Zn(1)–O(1) 2.072(1), Zn(1)–N(2) 2.080(1), K(1)–O(1) 3.037(1); bond angles (°): N(1)–Zn(1)–O(B) 101.99(6), N(1)–Zn(1)–O(1S) 102.19(6), O(1B)–Zn(1)–O(1S) 82.21(5), N(1)–Zn(1)–O(1) 162.63(6), O(1B)–Zn(1)–O(1) 95.29(7), O(1S)–Zn(1)–O(1) 81.75(5), N(1)–Zn(1)–N(2) 80.89(6), O(1B)–Zn(1)–N(2) 126.06(5), O(1S)–Zn(1)–N(2) 150.73(5), O(1)–Zn(1)–N(2) 87.55(5).

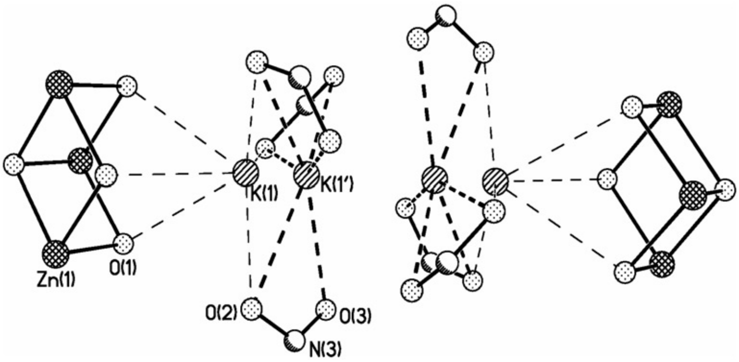


Figure 2. The scheme illustrating the general view of Zn_3O_3K cluster and dynamic disorder of potassium atoms.

Evidently, formation of the complex occurs by high electron-donor activity of oxygen atoms of the aldehyde of the Schiff-base ligand [1–7, 10–19] and the possibility of IA group metals to link metalloligands [20, 21]. Complex **4** is an example of self-assembled [22–24] pseudocuboid, heterotetranuclear structure. Search for similar structures in CCCD has not been successful.

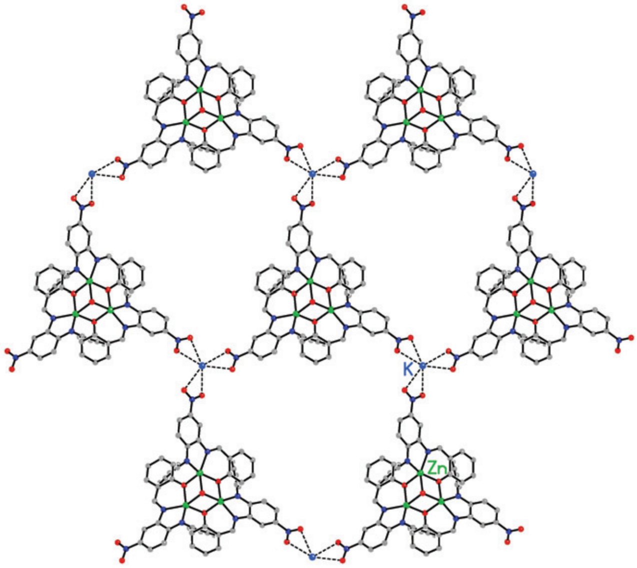


Figure 3. K . . . O bonded layer in a crystal of **4**. Anions are assembled by K(1') atoms.

4. Conclusion

We have synthesized an unusual self-assembled architecture constructed from a tetranuclear KZn_3 complex based on a tridentate dibasic Schiff base (**1**). Metallosupramolecular arrays are generally obtained by connecting appropriate ligands with metalloconnectors such as metal cations [25–27] and coordinatively unsaturated or labile low-molecular weight metallocomplexes [28, 29] with the formation of two- and three-dimensional macrocycles [26–29], helicates [30, 31], greeds [25, 30, 31], nanocages [26] and boxes [27]. Rhenium(I) tricarbonyl complexes were also used as connectors resulting in formation of triangular and square self-assembled complexes [32]. The peculiarity of **4** consists in combination of potassium cation and three neighboring nitro-groups as connectors. Similar situation was only observed when resorcarene dithiocarbamates were connected with Cu(II) or Zn(II) ions giving rise to molecular loop and molecular tetrahedron, respectively [33]. Such approaches may be expected as a source of numerous metallosupramolecular architectures.

Acknowledgments

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