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Synthesis, Crystal Structure, and Magnetic Characterization of Chiral Schiff-Base Manganese(III) Complex Containing Cocrystallized Crown Ether Molecule[1]

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Abstract—A chiral Schiff-base Mn(III) compound containing cocrystallized crown ether {Mn[(*R,R*)-Salcy]·$(H_2O)_2$}$_2(ClO_4)_2$·18-Crown-6 (**I**), where (R,R)-Salcy = (R,R)-N, *N*'-(1,2-cyclohexanediylethylene)bis(salicylideneiminato)dianion, has been synthesized by the reaction of {Mn[(*R,R*)-Salcy]$(H_2O)_2$}ClO_4 with 18-crown-6 ether and $K_4[Mo(CN)_8]$. X-ray diffraction analysis revealed that the cationic mononuclear Mn(III) Schiff-base compounds were self-complementary via intermolecular O–H···O H-bond formed by coordinated aqua ligand of one molecule and phenolic oxygen atoms of the neighboring molecule, giving supramolecular dimeric structure. The H-bond between O atoms of the cocrystallized crown molecule and that of the mentioned above dimer supported formation of one-dimensional supramolecular chain structure which can be linked to two-dimensional supramolecular network based on intermolecular O–H···Cl weak interactions. Our study of its magnetic properties revealed weak antiferromagnetic coupling between the adjacent Mn(III) ions.

Keywords: chiral Mn(III) Schiff-base, synthesis, crystal structure, magnetic properties

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INTRODUCTION

Over recent three decades magnetic molecular complexes attracted attention of research groups not only for the purpose of full elucidation of the nature of magnetic coupling, magneto-structural correlation, and some exotic magnetic phenomena but also their application in high-tech areas [1–4]. One of the most distinguished magnetic transferring groups the cyanide group demonstrates unique characteristics in the processes of preparing heterometallic molecular magnetic materials [5–9].

Among assembling segments used in synthesis of cyanide-bridged magnetic complexes, Mn(III)-salen (salen = N,N-ethylene-bissalicylideneiminate) complexes containing N_2O_2 equatorial salen-type ligands attracted close attention due to their facile preparation and high spin state ($S = 2$) as well as negative magnetic anisotropy of the central Mn(III) ions. Based on Mn(III)-salen types of compounds and various precursors containing different number of the cyanide group, many cyanide-bridged self-assemblies with a variety of structures ranging from discrete compounds and one-dimensional chains to two-dimensional networks have been reported [10].

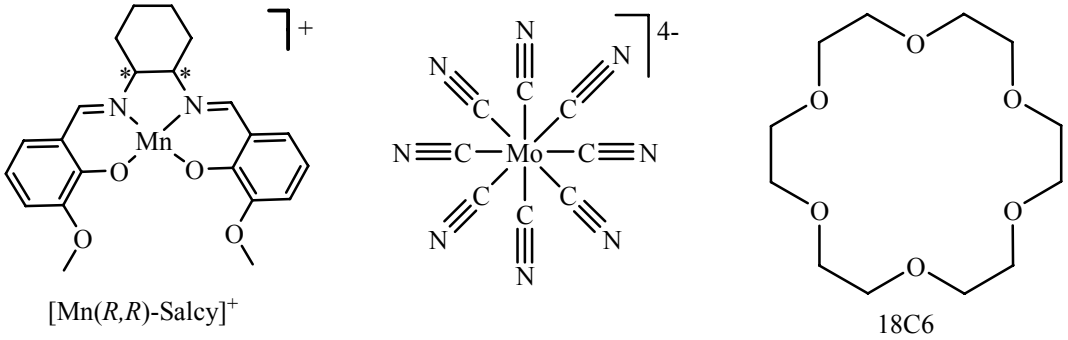
The current study is devoted to the reaction of chiral Schiff-base Mn(III) compound {Mn[(*R,R*)-Salcy]$(H_2O)_2$}ClO_4 with $K_4[Mo(CN)_8]$ (Scheme 1) in the presence of 18-crown-6 ether. Unexpectedly, its product was the chiral mononuclear Mn(III) containing complex combined with the cocrystallized crown ether. Synthesis, crystal structure and magnetic properties of the complex are presented in this paper.

EXPERIMENTAL

CHN elemental analysis was carried out with an Elementary Vario El. Variable-temperature magnetic susceptibility and field dependence magnetization measurements were performed on a Quantum Design MPMS SQUID magnetometer. The experimental

[1] The text was submitted by the authors in English.

Scheme 1. The starting compounds used



susceptibilities were corrected for the diamagnetism of the constituent atoms (Pascal's tables). The reaction was carried out under atmospheric pressure and all chemicals and solvents used were reagent grade without further purification. The product {Mn[(*R,R*)-Salcy]$(H_2O)_2$}ClO_4 was prepared as described for other manganese Schiff-base compounds [11].

Preparation of the complex I. A tube was charged with a solution of $K_4[Mo^{IV}(CN)_8]$ (0.1 mmol, 46 mg) and 18-crown-6 (0.4 mmol, 105.6 mg) in DMF (5 mL) followed by careful addition of a mixture of DMF and CH_3OH (ratio 1 : 2). A solution of {Mn[(*R,R*)-Salcy]·$(H_2O)_2$}ClO_4 (0.4 mmol, 204.4 mg) in 10 mL CH_3OH was carefully added to the top of the solvent layer. The tube was stored undisturbed in darkness. In one week time the block-like dark-brown crystals suitable for X-ray diffraction experiment were formed. The crystals were filtered off and dried in the air. Yield 117 mg (ca. 45.6%). Calculated, %:C 48.57; H 5.64; N 4.36. $C_{52}H_{72}Cl_2Mn_2N_4O_{22}$. Found, %: C 49.01; H 5.36; N 4.68.

X-Ray data and structure refinement. Single crystals of the complex **I** were mounted on the glass rod and X-ray crystal data were collected on a Bruker SMART CCD diffractometer with a MoK_α sealed tube (λ = 0.71073 Å) at 293 K using a ω scan mode. The structure was elucidated by direct method and expanded using Fourier difference techniques with the SHELXTL-97 program package [12]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced as fixed contributors and assigned isotropic displacement coefficients U(H) =1.2U(C) or 1.5U(C). Their coordinates were allowed to ride on the respective carbon atoms using SHELXL97. The CIF tables of the complex **I** have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 1040396. Details of the crystal parameters, data collection and refinement are presented in Table 1.

RESULTS AND DISCUSSION

Synthesis. According to the earlier reports [13–16] the Schiff-base Mn(III) compounds based on chiral cyclohexanediamine were good candidates for assembling chiral cyanide-bridged magnetic complexes. Synthetic approach to the new chiral cyanide-bridged complex was based on the reaction of

Table 1. Crystallographic data for the complex **I**

Value	Parameter
Chemical formula	$C_{52}H_{72}Cl_2Mn_2N_4O_{22}$
FW	1285.92
Crystal system	Triclinic
Space group	*P*1
a, Å	11.777(3)
b, Å	12.005(3)
c, Å	12.675(3)
α, deg	69.458(2)
β, deg	62.794(2)
γ, deg	72.992(3)
V, Å^3	1473.5(5)
Z	1
Completeness	98.9 %
F(000)	672
θ, deg	1.83–25.01
GOF	1.032
R_1 [$I > 2\sigma(I)$]	0.0470
wR_2 (all data)	0.1256

Table 2. Selected bond lengths (Å) and bond angles (deg) for complex **I**

Bond	*d*, Å	Angle	θ, deg
$Mn^1–N^1$	1.987(6)	$O^{17}–C^{41}$	1.383(12)
$Mn^1–N^2$	1.999(5)	$O^{17}–C^{51}$	1.435(12)
$Mn^1–O^9$	1.863(5)	$O^{18}–C^{49}$	1.447(13)
$Mn^1–O^{10}$	1.865(5)	$O^{18}–C^{50}$	1.367(12)
$Mn^1–O^{11}$	2.268(5)	$O^{19}–C^{47}$	1.397(10)
$Mn^1–O^{12}$	2.245(5)	$O^{19}–C^{48}$	1.349(14)
$Mn^2–N^3$	1.979(6)	$O^{20}–C^{52}$	1.375(12)
$Mn^2–N^4$	1.979(6)	$O^{20}–C^{46}$	1.409(12)
$Mn^2–O^{13}$	1.903(5)	$O^{21}–C^{44}$	1.436(11)
$Mn^2–O^{14}$	1.866(5)	$O^{21}–C^{45}$	1.289(15)
$Mn^2–O^{15}$	2.274(5)	$O^{22}–C^{43}$	1.320(12)
$Mn^2–O^{16}$	2.263(5)	$O^{22}–C^{42}$	1.481(15)
Angle	θ, deg	Angle	θ, deg
$O^9Mn^1N^1$	92.7(2)	$O^{14}Mn^2O^{13}$	93.0(2)
$O^{10}Mn^1N^1$	175.5(2)	$O^{14}Mn^2N^3$	174.3(2)
$O^9Mn^1N^2$	173.0(3)	$O^{13}Mn^2N^3$	92.2(2)
$O^{10}Mn^1N^2$	93.2(2)	$O^{14}Mn^2N^4$	92.0(2)
$N^1Mn^1N^2$	83.3(2)	$O^{13}Mn^2N^4$	174.0(3)
$O^9Mn^1O^{12}$	95.5(2)	$N^3Mn^2N^4$	82.9(2)
$O^9Mn^1O^{10}$	91.0(2)	$O^{14}Mn^2O^{16}$	93.5(2)
$O^{12}Mn^1O^{11}$	173.7(2)	$O^{16}Mn^2O^{15}$	174.9(2)

{Mn[(*R,R*)-Salcy](H$_2$O)$_2$}ClO$_4$ with K$_4$[Mo(CN)$_8$], which contained the maximum number of the cyanide groups in the polycyanometallate family. In our recent study [17] it had been determined that the reaction of K$_4$[W(CN)$_8$] carried out in organic solvent and 18-crown-6 resulted in formation of cyanide-bridged W–Ni complexes of the novel structural type [17]. The new complex containing the cocrystallized chiral Schiff-base manganese and crown ether was synthesized. It should be pointed out that no single crystals were formed upon slow evaporation of the solvents but entirely the mixture of {Mn[(*R,R*)-Salcy]·(H$_2$O)$_2$}ClO$_4$ and 18-crown-6 ether in methanol.

Crystal structure of complex I. Some important structural parameters for the complex **I** are presented in Table 2. The complex **I** crystallized in the triclinic space group *P*1, containing only one independent unit in the unit cell. The coordination sphere for the manganese ion was a distorted octahedral, in which four equatorial positions were occupied by the N_2O_2 unit of the Schiff-base ligand and the other two axial ones came from oxygen atoms of the coordinated water molecules. As tabulated in Table 2, the average distances between the Mn atom (with Mn^1 as representative) and the N, O atoms of the equatorial chelating Schiff-base ligand (1.993 and 1.864 Å) were clearly shorter than the Mn–O_{axial} bond lengths [2.268(5) and 2.245(5) Å], which presented information on elongation of octahedron surrounding of Mn(III) ion, typically accounted for the Jahn–Teller effect. Two mononuclear manganese Schiff-base entities (Fig. 2) were self-complementary via the intermolecular O–H···O hydrogen bond interactions between the coordinated aqua ligand of one molecule

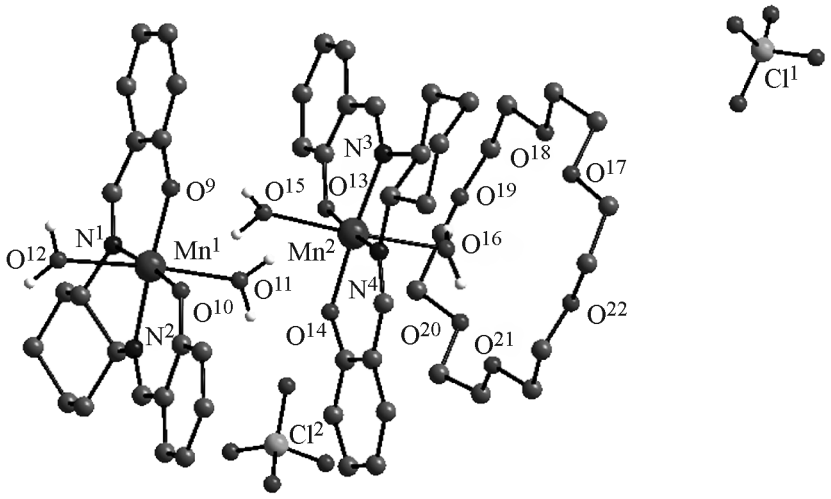


Fig. 1. The molecular structure of complex **I.** All H atoms except those on the coordinated water molecules are omitted for clarity.

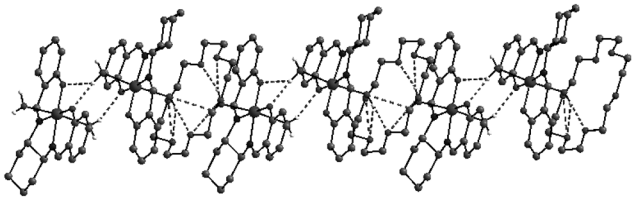


Fig. 2. The cationic one-dimensional supramolecular infinite structure of complex **I**. All H atoms except those on the coordinated water molecules and the balanced ClO_4^- ion are omitted for clarity.

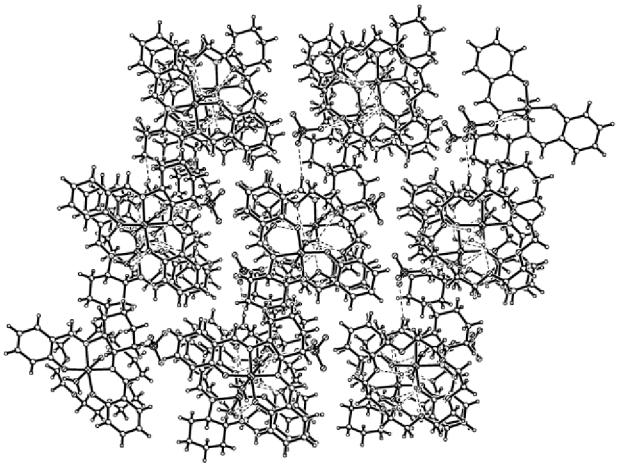


Fig. 3. The cell packing diagram along *a* axis of complex **I.**

and the phenolic oxygen atoms of the neighboring one, giving the supramolecular structure. Under the action of O–H···O_{18C6} hydrogen bond interactions and intermolecular O–H···Cl weak interactions the complex **I** could be linked to one- and two-dimensional suparmolecular structures (Figs. 2 and 3), respectively.

Magnetic properties of the complex I. The magnetic properties of the complex **I** have been studied. At room temperature the values of $\chi_M T$ (Fig. 4) were ca 6.13 emu mol^{-1} K that corresponded to two high spin Mn(III) ions with $S = 2$. Upon cooling, $\chi_M T$ remained constant down to ca 75 K, and then decreased steadily reaching ca 1.5 emu mol^{-1} K at 2 K.

Magnetic behavior of the complex could be due to one of the following reasons or a combination of those: (1) zero field splitting (D) of the ground state of Mn(III); (2) antiferromagnetic interaction between Mn (III) ions within the supramolecular dimer mediated by the H-bond for the latter. The magnetic susceptibility data for the complex **I** were simultaneously fitted in by full-matrix diagonalization of the following spin Hamiltonian [1]:

$$H = -2JS_1S_2 + D_1[S_{1z^2} - 1/3S_1(S_1 + 1)] + D_2[S_{1z^2} - 1/3S_2(S_2 + 1)].$$

Here equation the first term refers to the exchange interaction between Mn(III) ions within the supramolecular dimer. The second and third terms take into account the zero field splitting (ZFS) effects for two manganese ions ($D_1 = D_2$). In view of the axially elongated structure around Mn(III), the negative sign is expected for D [18]. Therefore, D was constrained to negative values in our calculations. The best set of parameters that matched the experimental data were found to be $J = -1.21$ cm^{-1}, $D = -0.68$ cm^{-1}, $g = 1.99$.

CONCLUSIONS

In summary, we have synthesized the new chiral Schiff-base Mn(III) and crown ether cocrystallized complex $[Mn((R,R)\text{-}3\text{-}MeOSalcy)(H_2O)_2]_2(ClO_4)_2 \cdot 18\text{-}Crown\text{-}6$ (**1**) in the reaction of $[Mn((R,R)\text{-}3\text{-}MeOSalcy)(H_2O)_2]ClO_4$ with 18-crown-6 ether and $K_4[Mo(CN)_8]$ in the orangnic solvent system. The study of magnetic properties of the complex **I** revealed the overall weak antiferromagnetic coupling between the adjacent Mn(III) ions.

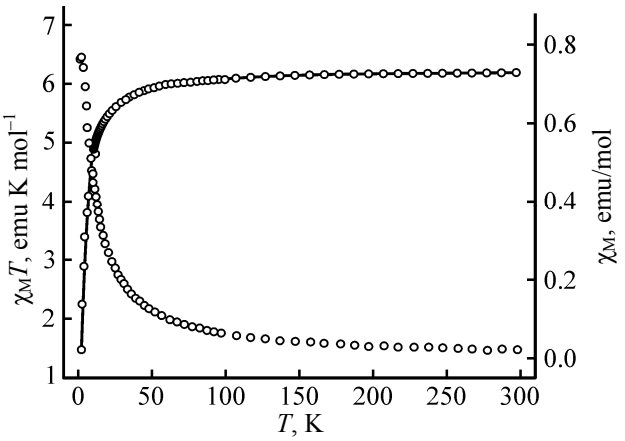


Fig. 4. χ_M vs T and $\chi_M T$ vs T curves for complex **I**. The solid lines represent to the best fit curve.

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REFERENCES

1. Kahn, O., *Molecular Magnetism.* Weinheim: VCH, 1993.
2. Sato, O., Kawakami, T., Kimura, M., Hishiya, S., Kubo, S., and Einaga, Y., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 41, p. 13176. DOI: 10.1021/ja046329s.
3. Berlinguette, C.P., Dragulescu-Andrasi, A., Sieber, A., Galan-Mascaros, J.R., Gudel, H.U., Achim, C., and Dunbar, K.R., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 20, p. 6222. DOI: 10.1021/ja039451k.
4. Shatruk, M., Dragulescu-Andrasi, A. Chambers, K.E., Stoian, S.A., Bominaar, E.L., Achim, C., and Dunbar, K.R., *J. Am. Chem. Soc.*, 2007, vol. 129, no. 19, p. 6104. DOI: 10.1021/ja066273x.
5. Wen, H.R., Wang, C.F., Li, Y.Z., Zuo, J.L., Song, Y., and You, X.Z., *Inorg. Chem.*, 2006, vol. 45, no. 1, p. 7032. DOI: 10.1021/ic060462z.
6. Kaneko, W. Kitagawa, S., and Ohba, M., *J. Am. Chem. Soc.* 2007, vol. 129, no. 2, p. 248. DOI: 10.1021/ja066140b.
7. Minguet, M., Luneau, D., Lhotel, E., Villar, V., Paulsen, C., Amabilino, D.B., and Veciana, J., *Angew. Chem., Int. Ed.*, 2002, vol. 41, no. 4, 586. DOI: 10.1002/1521-3773 (20020215).
8. Milon, J., Daniel, M.C., Kaiba, A., Guionneau, P., Brandès, S., and Sutter, L.P., *J. Am. Chem. Soc.*, 2007, vol. 129, no. 45, p. 13872. DOI: 10.1021/ja073612t.
9. Inoue, K., Kikuchi, K., Ohba, M., and Okawa, H., *Angew. Chem., Int. Ed.*, 2003, vol. 42, no. 1, p. 4709. DOI: 10.1002/anie.200390591.
10. Miyasaka, H., Saitoh, A., and Abe, S., *Coord. Chem. Rev.*, 2007, vol. 251, nos. 21–24, p. 2622. and references therein. doi:10.1016/j.ccr.2007.07.028.
11. Miyasaka, H., Matsumoto, N., Okawa, H., Re, N., Gallo, E., and Floriani, C., *J. Am. Chem. Soc.*, 1996, vol. 118, no. 5, p. 981. DOI: 10.1021/ja952706c.
12. Sheldrick, G.M., *SHELXS 97,* Program for the Solution of Crystal Structure, University of Göttingen, Göttingen, Germany, 1997.
13. Yao, M.X., Zheng, Q., Cai, X.M., Li, Y.Z., Song Y., and Zuo, J.L., *Inorg, Chem.*, 2012, vol. 51, no. 4, p. 2140. DOI: 10.1021/ic201982d.
14. Zhang, D.P., Bian, Y.Z., Qin, J., Wang, P., and Chen, X., *Dalton Trans.*, 2014, vol. 43, no. 3, p. 945. DOI: 10.1039/C3DT52996G.
15. Ru, J., Gao, F., Yao, M.X., Wu T., and Zuo, J.L., *Dalton Trans.*, 2014, vol. 43, no. 48, p. 18047. DOI: 10.1039/C4DT02518K.
16. Ru, J., Gao, F., Wu, T., Yao, M.X., Li Y.Z., and Zuo, J.L., *Dalton Trans.*, 2014, vol. 43, no. 3, p. 933. DOI: 10.1039/C3DT52951G.
17. Zhang, D.P., Zhang, L.F., Li, G.J., and Ni, Z. H., *Chem. Commun.*, 2013, vol. 49, no. 83, p. 9582. DOI: 10.1039/C3CC46063K.
18. Kennedy, B.J. and Murray, K.S., *Inorg. Chem.*, 1985, vol. 24, no. 10, p. 1552. DOI: 10.1021/ic00204a029.