

КРАТКИЕ СООБЩЕНИЯ

UDC 548.73:547.13:546.711

CRYSTAL STRUCTURE OF A Mn(II) COMPLEX WITH ISATIN-HYDRAZONE-S-BENZYLDTIIOCABAZATE

J.-J. Xia

School of Materials and Chemical Engineering Anhui University of Architecture, Hefei, P. R. China
E-mail: xiajj@aiai.edu.cn

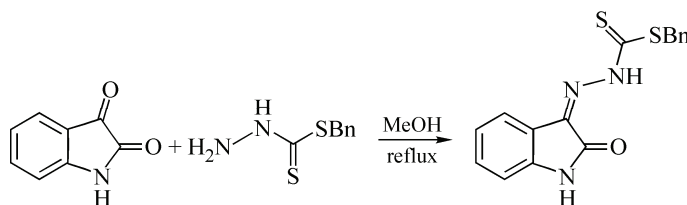
Received May, 9, 2012

The reaction of $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with isatin-hydrazone-S-benzylthiocarbamate (HIsa-SBn) results in the formation of a bis-ligand complex $[\text{Mn}(\text{Isa-SBn})_2] \cdot 2\text{DMF}$. Its single crystal is obtained and the structure is determined by X-ray diffraction. It belongs to a monoclinic space group $C2/c$ with the cell parameters: $a = 23.290(4) \text{ \AA}$, $b = 11.4980(18) \text{ \AA}$, $c = 18.483(5) \text{ \AA}$, $V = 4087.6(14) \text{ \AA}^3$. The Mn(II) atom is six-coordinated with two amide O atoms, two azomethine N atoms, and two thiolate S atoms, resulting in a distorted octahedral geometry.

Keywords: X-ray diffraction, dithiocarbamate, isatin, manganese(II) acetate.

S-alkyl/aryl dithiocarbamate ester-containing Schiff bases [1–5] have been the subject of considerable studies due to their hard N and soft S donor atoms which enable the Schiff bases to easily coordinate with transition state metals. These metal complexes have been found to exhibit interesting physicochemical properties [6] and biological activities [7]. The isatin-containing Schiff bases introduce a third amide O donor, which further facilitates metal chelation [8–10], and some of the metal complexes have been synthesized and characterized [11]. Herein, a new Mn(II) coordinated complex is synthesized from $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and isatin-hydrazone-S-benzylthiocarbamate and its crystal structure is revealed.

Experimental. Synthesis of isatin-hydrazone-S-benzylthiocarbamate (HIsa-SBn). Isatin (5.0 mmol) and S-benzylthiocarbamate (5.0 mmol) are dissolved in 50 ml of methanol; this solution is refluxed for 30 min before cooling for overnight. The precipitates are collected by filtration to give the crude product which is recrystallized from acetonitrile to obtain the desired pure product as yellow crystals with a yield of 85 % (Scheme 1).



Scheme 1. Synthesis of isatin-hydrazone-S-benzylthiocarbamate

Synthesis of $[\text{Mn}(\text{Isa-SBn})_2] \cdot 2\text{DMF}$. $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (1.0 mmol) dissolved in hot methanol (10 ml) is added to a boiling solution of HIsa-SBn (2.0 ml) in acetonitrile (50 ml). This solution is refluxed for 2 h before cooling overnight. The precipitates are collected by filtration, washed with

Table 1

Crystal data and structure refinement for the complex

Chemical formula	C ₃₈ H ₃₈ MnN ₈ O ₄ S ₄
Molecular weight	853.94
Crystal system	Monoclinic
Space group	<i>C</i> 2/ <i>c</i>
<i>a</i> , <i>b</i> , <i>c</i> , Å	23.290(4), 11.4980(18), 18.483(5)
β, deg.	124.325(2)
<i>T</i> , K	296(2)
<i>V</i> , Å ³	4087.6(14)
<i>Z</i>	4
<i>D</i> _c , g·cm ⁻³	1.388
μ, mm ⁻¹	0.577
<i>F</i> (000)	1772
θ range, deg.	2.3/27.6
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	-27/27, -13/13, -21/21
<i>R</i> _{int}	0.0244
Refined data, parameter, restriction	3605, 251, 0
Observed reflections with <i>I</i> > 2σ(<i>I</i>)	2824
GOOF	1.058
Final <i>R</i> factor [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0338, <i>wR</i> ₂ = 0.0913
<i>R</i> factor (all data)	<i>R</i> ₁ = 0.0471, <i>wR</i> ₂ = 0.0982

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|.$$

$$^b wR_2 = \sum w(|F_o|^2 - |F_c|^2) / \sum w(F_o)^2)^{1/2}, \text{ where } w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP].$$

$$P = (F_o^2 + 2F_c^2)/3.$$

Table 2

Selected geometric parameters (Å, deg.)

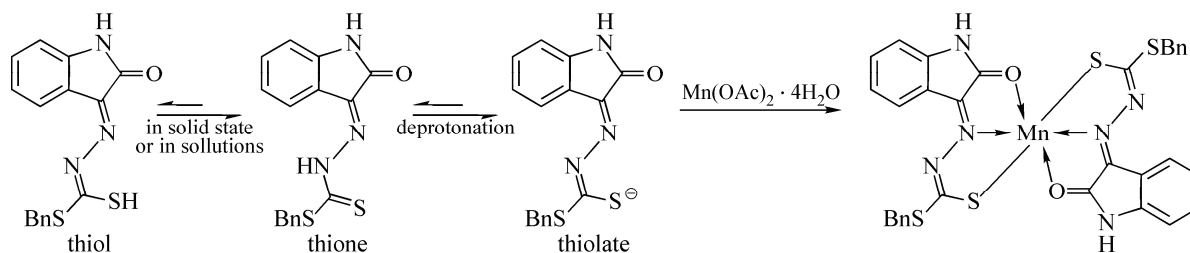
Mn1—N2	2.2066(16)	Mn1—O1	2.4126(16)	Mn1—S1	2.5300(7)
C7—S2	1.823(2)	C8—N1	1.310(3)	C8—S1	1.710(2)
C8—S2	1.755(2)	C9—N2	1.289(3)	C9—C19	1.486(3)
C19—O1	1.237(2)	C19—N3	1.343(3)	N1—N2	1.366(2)
N2—Mn1—O1	84.56(6)	N2—Mn1—S1	75.87(5)	O1—Mn1—S1	88.86(4)
N1—C8—S1	129.66(15)	N1—C8—S2	115.68(14)	S1—C8—S2	114.64(12)
C8—S2—C7	101.16(11)	C8—S1—Mn1	95.49(7)	C8—N1—N2	112.40(15)
C9—N2—N1	117.29(16)	C9—N2—Mn1	118.20(12)	N1—N2—Mn1	124.50(13)
N2—C9—C19	115.92(17)	O1—C19—C9	124.2(2)	N3—C19—C9	107.52(17)

methanol, and dried over vacuum. The desired crystal is obtained by slowly evaporating the precipitate from a mixture solution of DMF and methanol.

X-ray crystallography. A Bruker Smart Apex II CCD area-detector diffractometer is used for the crystallographic data collections with graphite monochromated MoK_α radiation (λ = 0.71073 Å) at 296(2) K using the ω-scan technique. The diffraction data were integrated using the SAINT program

[12], which was also used for the intensity corrections for the Lorentz and polarization effects. Semi-empirical absorption correction was applied using the SADABS program [13]. The structures were solved by direct methods and all the non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [14]. Hydrogen atoms were generated geometrically. Tables 1 and 2 list the data for the details of crystal parameters and selected bond lengths and angles respectively.

Results and discussion. Isatin-hydrazone-S-benzylthiocarbazate (HIsa-SBn) can tautomerize into its thiol forms (Scheme 2) as most other thiosemicarbazones [15]. The thione state is confirmed to be predominant in both solid state and solutions [11]. However, if deprotonated, the thiolate form makes major contributions, which further reacts with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ to give the Mn(II) complex.

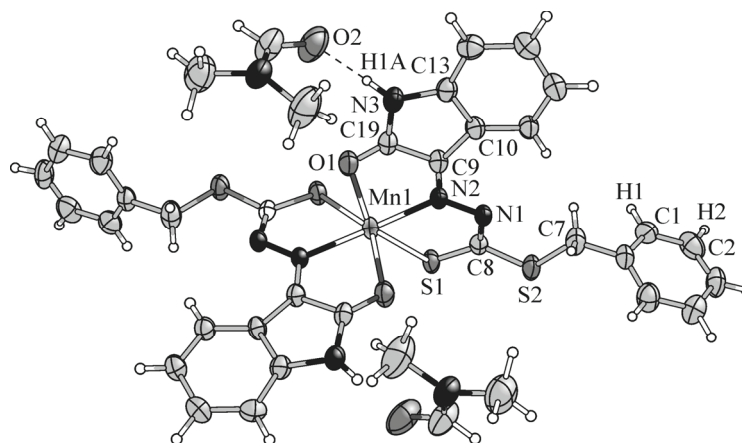


Scheme 2. Thiol, thione, and thiolate forms of HIsa-SBn and the subsequent reaction with $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ to give the Mn(II) complex

Fig. 1 displays the Mn(II) complex in a monoclinic crystal system and the $C2/c$ space group. In this complex, each HIsa-SBn ligand is tri-chelated with the Mn(II) atom, making Mn(II) to be six-coordinated, resulting in a distorted octahedral geometry. For the chelation patterns of Mn(II) with heteroatoms, Mn1—S1 is a typical covalent bond with the distance to be only 2.5300(7) Å, while Mn1—O1 and Mn1—N2 bond distances are 2.4126(16) Å and 2.2066(16) Å respectively, indicating that O1 and N2 are chelated with Mn(II).

Three intermolecular hydrogen bonds are found to be N3—H1A \cdots O2, C1—H1 \cdots O2', and C2—H2 \cdots O1', of which the latter two hydrogen bonds have the symmetry codes $1/2-x, -1/2+y, 1/2-z$ and $x, 1-y, -1/2+z$. For N3—H1A \cdots O2, N3—H1A, H1A \cdots O2, and N3 \cdots O2 distances are 0.93 Å, 1.89 Å, and 2.802(4) Å; the bond angle is found to be 168°. As for C1—H1 \cdots O2', the corresponding C1—H1, H1 \cdots O2', and C1 \cdots O2' bond lengths are 0.93 Å, 2.50 Å, and 3.434(4) Å respectively. The C1—H1 \cdots O2' bond angle is 171°. For the third one of C2—H2 \cdots O1', the corresponding values are found to be 0.93 Å, 2.59 Å, and 3.511(4) Å for bond lengths and 172° for the bond angle. Besides, possible $\pi\cdots\pi$ weak interactions between the neighboring isatin group and the benzyl group are found to be too weak to be considered.

Fig. 1. Molecular structure of the titled compound with the atom numbering scheme. Displacement ellipsoids are drawn at the 30 % probability level



Supplementary material. CIF file containing complete information on the studied structure was deposited with CCDC, deposition number 880715, and is freely available upon request from the following web site: http://www.ccdc.cam.ac.uk/data_request/cif

This work is financially supported by the Anhui Provincial Natural Science Foundation (No. 1208085QB24).

REFERENCES

1. Ali M.A., Mirza A.H., Ravoof T.B.S.A., Bernhardt P.V. // *Polyhedron*. – 2004. – **23**. – P. 2031; (b) Ali M.A., Mirza A.H., Ravoof T.B.S.A., Bernhardt P.V. // *Polyhedron*. – 2004. – **23**. – P. 2037.
2. Ali M.A., Mirza A.H., Voo C.W., Tan A.L., Bernhardt P.V. // *Polyhedron*. – 2003. – **22**. – P. 3433; (b) Ali M.A., Mirza A.H., Nazimuddin M., Ahmed R., Gahan L.R., Bernhardt P.V. // *Polyhedron*. – 2003. – **22**. – P. 1471; (c) Ali M.A., Mirza A.H., Keng S.T.W., Butcher R.J. // *Transition Met. Chem.* – 2003. – **28**. – P. 241.
3. Ali M.A., Mirza A.H., Butcher R.J., Tarafder M.T.H., Keat T.B., Ali A.M. // *J. Inorg. Biochem.* – 2002. – **92**. – P. 141; (b) Ali M.A., Mirza A.H., Nazimuddin M., Rahman H., Butcher R.J. // *Transition Met. Chem.* – 2002. – **27**. – P. 268; (c) Ali M.A., Mirza A.H., Nazimuddin M., Dhar P.K., Butcher R.J. // *Transition Met. Chem.* – 2002. – **27**. – P. 27; (d) Ali M.A., Mirza A.H., Butcher R.J., Tarafder M.T.H., Ali M.A. // *Inorg. Chim. Acta.* – 2001. – **320**. – P. 1.
4. Crouse K.A., Chew K.-B., Tarafder M.T.H., Kasbollah A., Ali A.M., Yamin B.M., Fun H.-K. // *Polyhedron*. – 2004. – **23**. – P. 161; (b) Crouse K.A., Chew K.-B., Yamin B.M., Ng S.-W., Tarafder M.T.H. // *Acta Crystallogr., Sect. E*. – 2003. – **59**. – P. 148.
5. Shi Y.-C., Yang H.-M., Song H.-B., Yan C.-G., Hu X.-Y. // *Polyhedron*. – 2004. – **23**. – P. 567; (b) Zelenin K.N., Bezhan I.P., Ershov B.A., Zelenin A.K. // *Tetrahedron*. – 1994. – **50**. – P. 1147; (c) Wang W., Zeng F.L., Wang X., Tan M.Y. // *Polyhedron*. – 1996. – **15**. – P. 1699.
6. Tian Y.-P., Duan C.-Y., Zhao C.-Y., You X.-Z., Mak T.C.W., Zhang Z.Y. // *Inorg. Chem.* – 1997. – **36**. – P. 1247; (b) Liu Z.-H., Duan C.-Y., Hu J. // *Inorg. Chem.* – 1999. – **38**. – P. 1719; (c) Liu Z.-H., Yang S.-R., Duan C.-Y., You X.-Z. // *Chem. Lett. Jpn.* – 1999. – **10**. – P. 1063; (d) Tian Y.-P., Duan C.-Y., You X.-Z., Mak T.C.W., Luo Q., Hou J.-Y. // *Transition Met. Chem.* – 1998. – **23**. – P. 17; (e) Abu-Raqabah A., Davies G., El-Sayed M.A., El-Toukhy A., Shaikh S.N., Zubietta J. // *Inorg. Chim. Acta.* – 1992. – **193**. – P. 43.
7. Liberta A.E., West D.X. // *BioMetals*. – 1992. – **5**. – P. 121; (b) Ferrari M.B., Bisceglie F., Fava G.G., Pelosi G., Tarasconi P., Albertini R., Pinelli S. // *J. Inorg. Biochem.* – 2002. – **89**. – P. 36.
8. Rodriguez-Arguelles M.C., Sanchez A., Ferrari M.B., Fava G.G., Pelizzi C., Pelosi G., Albertini R., Lunghi P., Pinelli S. // *J. Inorg. Biochem.* – 1999. – **73**. – P. 7.
9. Ferrari M.B., Pelizzi C., Pelosi G., Rodriguez-Arguelles M.C. // *Polyhedron*. – 2002. – **21**. – P. 2593.
10. Bacchi A., Cracelli M., Pelagatti P., Pelizzi G., Rodriguez-Arguelles M.C., Rogolino D., Solinas C., Zani F. // *J. Inorg. Biochem.* – 2005. – **99**. – P. 397.
11. (a) Ali M.A., Bakar H.J.H.A., Mirza A.H., Smith S.J., Gahan L.R., Bernhardt P.V. // *Polyhedron*. – 2008. – **27**. – P. 71; (b) Ali M.A., Mirza A.H., Bakar H.J.H.A., Bernhardt P.V. // *Polyhedron*. – 2011. – **30**. – P. 556.
12. SAINT, version 6.02a; Bruker AXS Inc.: Madison, WI, 2002.
13. Sheldrick G.M. SADABS, Program for Bruker Area Detector Absorption Correction. – Germany, University of Göttingen, 1997.
14. (a) Sheldrick G.M. SHELXS-97, Program for Crystal Structure Solution. – Germany, University of Göttingen, 1997. (b) Sheldrick G.M. SHELXL-97, Program for Crystal Structure Refinement. – Germany, University of Göttingen, 1997.
15. Ali M.A., Nazimuddin M., Saha R., Butcher R.J., Bryan J.C. // *Polyhedron*. – 1998. – **17**. – P. 3955.