ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2010, Vol. 36, No. 3, pp. 226–231. © Pleiades Publishing, Ltd., 2010.

Synthesis, Characterization, and Crystal Structures of Two Novel Ion-Pair Complexes Based on Benzene-1,2-Dithiolate Ligand[1]

G. X. Liu[a, *], Y. Liu[a], S. Nishihara[b], and X. M. Ren[a]

[a] *Anhui Key Laboratory of Functional Coordination Compounds, School of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246003, PR. China*

[b] *Department of Physical Science, Graduate School of Science, Osaka Prefecture University Sahai, Osaka 599-8531, Japan*

**E-mail: liugx@live. com*

Received June 27, 2009

Abstract—Two novel ion-pair complexes, [IBzPy][Ni(Bdt)$_2$] (**I**) and [IBzDMPy][Ni(Bdt)$_2$] (**II**) (IBzPy = 1-(4-iodobenzyl)pyridinium, IBzDMPy = 1-(4-iodobenzyl)-3,5-dimethyl-pyridinium, and Bdt = benzene-1,2-dithiolate), have been synthesized and characterized by elemental analysis, IR, cyclic voltammetry, and X-ray single-crystal structure determination. The crystal structure determination reveals that the central Ni atoms in complexes **I** and **II** are in slightly distorted square-planar coordination environment. The cyclic voltammetric studies show that there are two oxidation peaks for complexes **I** and **II**, which are attributed to Ni(IV/III) and Ni(III/II) redox couples.

DOI: 10.1134/S1070328410030103

INTRODUCTION

Metal complexes of 1,2-dithiolate ligands have been intensively studied because of their novel properties and applications in the areas of molecular conducting, magnetic materials, nonlinear optics, and others [1, 2], Over the last decade, a large number of new dithiolene ligands and resultant complexes have been prepared to optimize the molecular properties in an effort to prepare novel and advanced material, whose molecular arrangement can be sensitively affected by strong and directional noncovalent interactions [3–6]. Although the closed-shell cations make no contribution to the conductivity and magnetism, their size and shapes play a predominant role in influencing the crystal structure and, consequently, in altering the electronic and magnetic properties. Physical properties of molecular conductors depend on the molecular alignment in crystals. On the one hand, unfortunately, the prediction of the molecular alignment within crystal is usually difficult because of the presence of many local minima of lattice energy derived from van der Waals interaction, which operates weakly and rather isotropically. On the other hand, intermolecular interactions, such as hydrogen bonds, S···S contacts, and $\pi \cdots \pi$ stacking are efficient organizing forces in supramolecular architecture and design of new solid-state materials for applications. Many research groups have succeeded in the strategy to control organic molecular aggregation by hydrogen bonding [7–9] and to synthesize organic conductors assembled by $\pi \cdots \pi$ stacking [10–12] or S···S contacts [13–17]. The unique physical properties of these complexes not only depend on the specific properties of the individual components but also are strongly influenced by the arrangement of molecules within the crystal lattice.

Recently, using benzylpyridinium derivatives ([RBzPy]$^+$) as the counter-cation of [M(Mnt)$_2$]$^-$ (M = Ni, Pd, and Pt; Mnt^{2-} = maleonitriledithiolate), a series of ion-pair complexes with segregated columnar stacks of cations and anions have been reported [18–22]. The quasi-one-dimensional magnetic nature of these complexes was attributed to intermolecular π-orbital interactions within the anionic columns. Furthermore, for some complexes, spin-Peierls-like transition was observed [18, 19]. More presently, we are devoted to our research interesting on the molecular magnets self-assemblied from [Ni(Bdt)$_2$]$^-$ ion due to its molecular and electronic structure resembling [Ni(Mnt)$_2$]$^-$ ion, which is expected to obtain new series of molecular magnets with peculiar magnetic phase transition via incorporating the benzylpyridinium derivatives into the [Ni(Bdt)$_2$]$^-$ spin system. Herein, we report synthesis, characterization, and crystal structures of two novel complexes consisting of [Ni(Bdt)$_2$]$^-$ and benzylpyridinium derivatives: [IBzPy][Ni(Bdt)$_2$] (**I**) and [IBzDMPy][Ni(Bdt)$_2$] (**II**) (IBzPy = 1-(4-iodobenzyl)pyridinium, IBzDMPy = 1-(4-iodobenzyl)-3,5-dimethylpyridinium and Bdt = benzene-1,2-dithiolate).

---

[1] The article is published in the original.

EXPERIMENTAL

All commercially available chemicals are of reagent grade and used as received without further purification. Benzene-1,2-dithiol was purchased from TCI Chemicals; [IBzPy]Br and [IBzDMPy]Br were synthesized following the published procedure [23]. Elemental analyses were determined using a Vario EL III elemental analyzer. IR spectra were recorded in the 4000–400 cm^{-1} region using KBr pellets and a Nicolet AVATAR-360 spectrometer. Cyclic voltammograms were recorded on an EG&G potentiostat/galvanostat model 273 analyzer in a one-compartment cell. The glassy-carbon working electrode, Pt counter electrode, and Ag–AgCl reference electrode were used under Ar atmosphere at 25°C in MeCN solution with approximately 0.1 M $[Bu_4N]ClO_4$ as conducting electrolyte. In the −1.2 to +1.2 V regions a potential scan rate of 100 mV s^{-1} was used.

Synthesis of $[IBzPy][Ni(Bdt)_2]$ (I). Under argon atmosphere at room temperature, benzene-1,2-dithiol (284 mg, 2 mmol) was added to a solution of sodium metal (92 mg, 4 mmol) in 25 ml of absolute methanol. A solution of $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) in methanol was added, resulting in the formation of a muddy red-brown color. Following this, [IBzPy]Br (752 mg, 2 mmol) was added, and the mixture allowed to stand with stirring for 1 h and then stirred for 24 h in air. The color of the mixture gradually turned green, indicating oxidation from a dianionic species to the more stable monoanionic form. The precipitate was washed with absolute methanol and ether and then dried. The crude product was recrystallized twice from methylene chloride to give black needles in ~68% yield.

IR (KBr; ν, cm^{-1}): 3041 w, 2957 s, 2856 m, 1485 s, 1421 s, 1225 m, 739 m, 667 s.

For $C_{24}H_{19}NIS_4Ni$

anal. calcd., %:	C, 45.36;	H, 3.01;	N, 2.20.
Found, %:	C, 45.33;	H, 3.07;	N, 2.18.

Synthesis of $[IBzDMPy][Ni(Bdt)_2]$ (II). The synthesis of complex II followed the similar procedure as for complex I except using [IBzDMPy]Br instead of [IBzPy]Br. The yield was 57%.

IR (KBr; ν, cm^{-1}): 3030 w, 2923 m, 1631 m, 1589 w, 1498 s, 1417 s, 1402 w, 1292 s, 1235 m, 1081 m, 1005 m, 928 w, 746 s, 730 s, 674 m.

For $C_{26}H_{23}NIS_4Ni$

anal. calcd, %:	C, 47.08;	H, 3.49;	N, 2.11.
Found, %:	C, 47.05;	H, 3.52;	N, 2.09.

X-ray diffraction analysis. Single-crystal data for complexes **I** and **II** were obtained on a Bruker Smart Apex II CCD with graphite-monochromated MoK_α a radiation (λ = 0.71073 Å) at 296(2) K using the ω scan technique. The data were integrated by using the SAINT program [24], which was also used for the intensity corrections for the Lorentz and polarization effects. An empirical absorption correction was applied using the SADABS program [25]. The structures were solved by direct methods using the program SHELXS-97 [26], and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package [27]. The hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELTXL crystallographic software package [27]. The details of the crystal parameters, data collection, and refinements for the complexes are summarized in Table 1. Selected bond lengths and bond angles with their estimated standard deviations are listed in Table 2. Atomic coordinates and other structural parameters of the complexes have been deposited with the Cambridge Crystallographic Data Center (nos. 695404 (**I**) and 695405 (**II**); deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The X-ray structural analysis of **I** reveals that the asymmetry unit contains a couple of $[Ni(Bdt)_2]^-$ anion and $[IBzPy]^+$ cation as depicted in Fig. 1a. The Ni-S distances range from 2.1432(16) to 2.1646(16) Å, with an average of 2.1459(16) Å, and the *cis*-SNiS angles range from 85.59(6)° to 91.96(6)°; the NiS_4 coordination thus adopts a slightly distorted square-planar configuration. Both of the coordinated Bdt^{2-} anions are closer to the planar geometry compared to other salts [28, 29], but $[Ni(Bdt_2)]^-$ anion as a whole is quasi-planar with Ni as the twist center, there exists the dihedral angle of 10.16° between the planes of the two coordinated Bdt^{2-} ligands. In the $[IBzPy]^+$ cation, the dihedral angles of the N(1)C(19)C(16) reference plane are 73.96° for the phenyl ring and 34.11° for the pyridine ring, respectively. The phenyl ring and the pyridine ring make a dihedral angle of 89.20°.

As illustrated in Fig. 2, in the crystal of **I**, the anions and cations are more or less parallel to each other. The dihedral angle between the pyridine ring of the cation and the plane of the anion is 2.1°. The interplanar distance between the plane through the anion and the plane through the cation, lying between two anions, is about 3.652 Å, and that between the cation and the anion is about 3.720 Å, which are close enough to conclude that the cations do have some π-stacking interaction with the acceptor anionic molecules. This means that two π–π interactions of different strength exist in a crystal. Moreover, C–H···S intermolecular contacts between the anion and the cation in **I** are further consolidate the structure. The most prominent general structural features of the complex are the completely segregated stacked columns of $[Ni(Bdt)_2]^-$ anions and $[IBzPy]^+$ cations, as revealed by the projection along the crystallographic *x* axis shown in Fig. 3a. The Ni···Ni distances is 6.199 Å within the column.

Table 1. Crystallographic parameters and a summary of data collection and refinement for structures **I** and **II**

Parameter	Value	
	I	**II**
M	635.25	663.30
Size, mm	0.36 × 0.20 × 0.04	0.26 × 0.12 × 0.10
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	16.073(4)	7.4020(12)
b, Å	8.540(2)	12.624(2)
c, Å	17.776(5)	14.290(2)
α, deg		91.285(2)
β, deg	92.327(3)	92.270(2)
γ, deg		98.459(2)
V, Å^3	2438.0(11)	1319.2(4)
Z	4	2
ρ_{calcd}, mg m^{-3}	1.731	1.670
F(000)	1260	662
θ, deg	2.29–25.00	1.63–25.05
Reflections collected	11514	6488
Independent reflections	4215 ($R_{int} = 0.0695$)	4522 ($R_{int} = 0.0240$)
Parameters	280	303
Goodness-of-fit on F^2	1.020	1.087
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0799$, $wR_2 = 0.2015$	$R_1 = 0.0539$, $wR_2 = 0.1833$
R indices (all data)	$R_1 = 0.0913$, $wR_2 = 0.2164$	$R_1 = 0.0712$, $wR_2 = 0.2117$
Large diff. peak and hole, e Å^{-3}	1.879/–1.563	1.157/–1.032

$R_1 = S||F_o| - |F_c||/S|F_o|$. $wR_2 = |Sw(|F_o|^2 - |F_c|^2)|/S|w(F_o)^2|^{1/2}$, $w = 1/[s^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Selected bond lengths and angles in structures **I** and **II**

Bond	d, Å	Bond	d, Å
		I	
Ni(1)–S(1)	2.1646(16)	Ni(1)–S(2)	2.1432(16)
Ni(1)–S(3)	2.1554(16)	Ni(1)–S(4)	2.1566(16)
		II	
Ni(1)–S(1)	2.1410(17)	Ni(1)–S(2)	2.1466(16)
Ni(2)–S(3)	2.1363(17)	Ni(2)–S(4)	2.1597(18)
Angle	ω, deg	Angle	ω, deg
		I	
S(1)Ni(1)S(2)	91.75(6)	S(1)Ni(1)S(3)	177.39(7)
S(1)Ni(1)S(4)	88.97(6)	S(2)Ni(1)S(3)	87.59(6)
S(2)Ni(1)S(4)	173.70(7)	S(3)Ni(1)S(4)	91.96(6)
		II	
S(1)Ni(1)S(2)	92.26(6)	S(3)Ni(2)S(4)	91.74(7)

The nearest Ni···Ni contact between $[Ni(Dmit)_2]^-$ columns is much longer at 8.540 Å and is longer than the Ni···Ni distance within the $[Ni(Bdt)_2]^-$ column.

It is interesting to find that, when $[IBzDMPy]^+$ with two methyl groups in the pyridine ring was introduced as countercation, complex **II** with different structures was obtained. As shown in Fig. 1b, the asymmetric unit of **II** contains two different, independent halves of centrosymmetric $[Ni(Bdt)_2]^-$ anions and one $[IBzDMPy]^+$ cation. The nickel atoms are each surrounded by four sulfur atoms in square-planar geometry. As for the Ni(1)-containing unit, the Ni(1)-S(1) and Ni(1)-S(2) distances are 2.1410(17) and 2.1466(16) Å, respectively (Table 2). The values are in agreement with the analogous $[Ni(Bdt)_2]^-$ complex reported [28, 29]. The S-Ni-S bond angle within the five-member ring is 92.26(6)°, which is slightly larger than that observed in the complex with substituent groups on benzene rings [28, 29]. There exists a dihedral angle of 3.08° between C(1)C(2)C(3)C(4)C(5)C(6)S(1)S(2) (C_6S_2) and the Ni(1)S(1)S(2) planes, so the anion adopts an envelope conformation and the Ni(1) atom deviates by 0.092 Å from the C_6S_2 plane. In Ni(2)-containing unit, the Ni–S bonds cover the range from 2.1363(17) to 2.1597(18) Å and the SNiS bond angle within the five member ring is 91.74(7)°, which is in agreement with that of the Ni(1)-containing unit. The Ni(2) atom deviates by 0.025 Å from the C(7)C(8)C(9)C(10)C(11)C(12)S(3)S(4) plane and the angle between C_6S_2 and the Ni(2)S(3)S(4) planes is 1.21°. The Ni(1)C_6S_2 and Ni(2)C_6S_2 planes are nearly perpendicular to each other with a dihedral angle of 89.36°. In the $[IBzDMPy]^+$, the dihedral

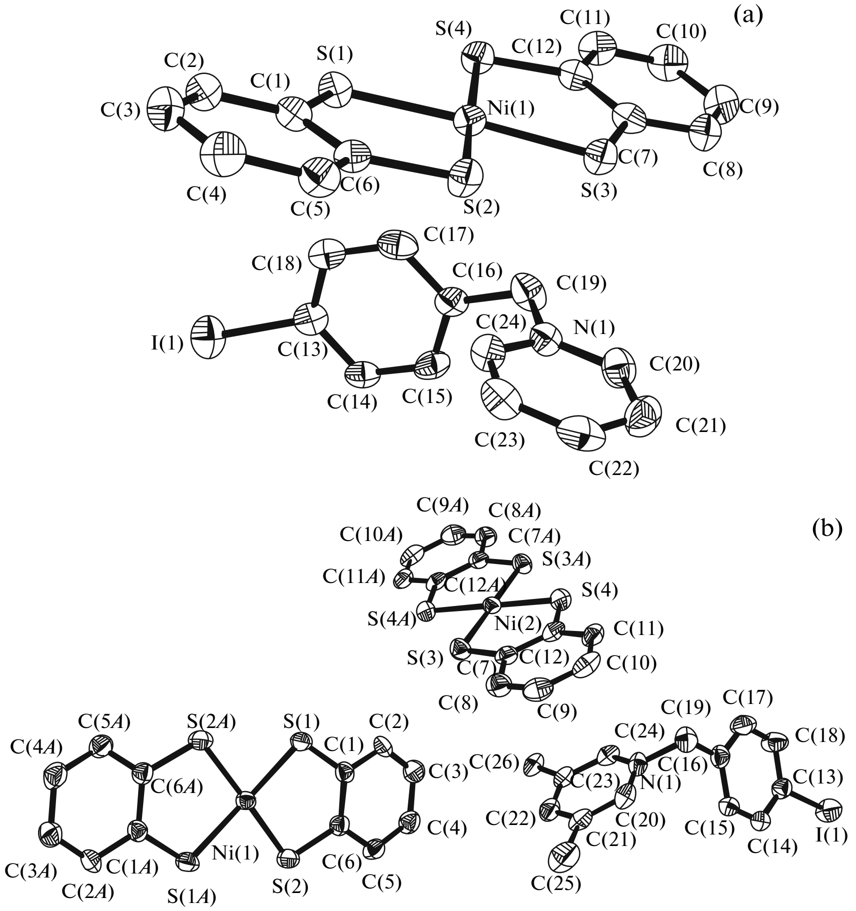

Fig. 1. ORTEP representation of **I** (a) and **II** (b) showing local coordination environment of Ni(III) with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity.

angles of the N(1)C(19)C(16) reference plane are 48.52° for the phenyl ring and 70.05° for the pyridine ring, respectively. The phenyl ring and the pyridine ring make a dihedral angle of 85.97°.

The molecule packings of two anionic units in **II** differ from each other (Fig. 1b). The Ni(1)-containing units stack in face-to-face fashion with an alternating arrangement of the $[Ni(Bdt)_2]^-$ anion and $[IBzDMPy]^+$ cation, so that the pyridine ring moiety of the cation lies above the phenyl ring moiety of the corresponding Ni(2)-containing units and vice versa, and the shortest distance between adjacent Ni^{3+} ions is 7.402 Å. Conversely, the Ni(1)-containing units stack in side-by-side fashion in which the anions with uniform spaced arrangements form one-dimensional (1D) chain along the *x* axis. The shortest distance between adjacent Ni^{3+} ions is 7.402 Å too. Between the most adjacent Ni(1)-containing and Ni(2)-containing units, a Ni···Ni distance of 9.427 Å is found. The Ni-containing anion and $[IBzDMPy]^+$ cation are held together via abnormal C(19)–H(19*A*)···S ($x, -1 + y, z$) H-bonding interactions and I(1)···S(3 ($1 + x, 1 - y, z$) weak interactions to consolidate the structure (Fig. 3b).

The cyclic voltammograms of **I** and **II** display two quasi-reversible one-electron redox processes. As an example, Fig. 4 shows the CV curve of **I**, and the half-wave potentials versus Ag/AgCl are 268 mV ($\Delta E = 111$ mV) and –311 mV ($\Delta E = 91$ mV), respectively. The former wave is assigned to the redox couple of $[Ni(Bdt)_2]^{-/0}$, and the later is attributed to the redox couple of $[Ni(Bdt)_2]^{-/2-}$. For **II**, the corresponding half-wave potentials versus Ag/AgCl are 272 mV ($\Delta E =$

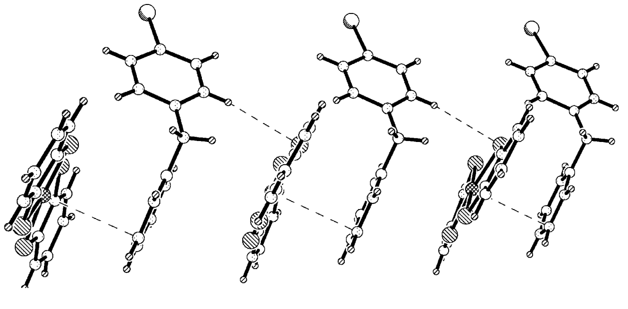

Fig. 2. C-C–H···S intermolecular contacts between the anion and the cation in **I**.

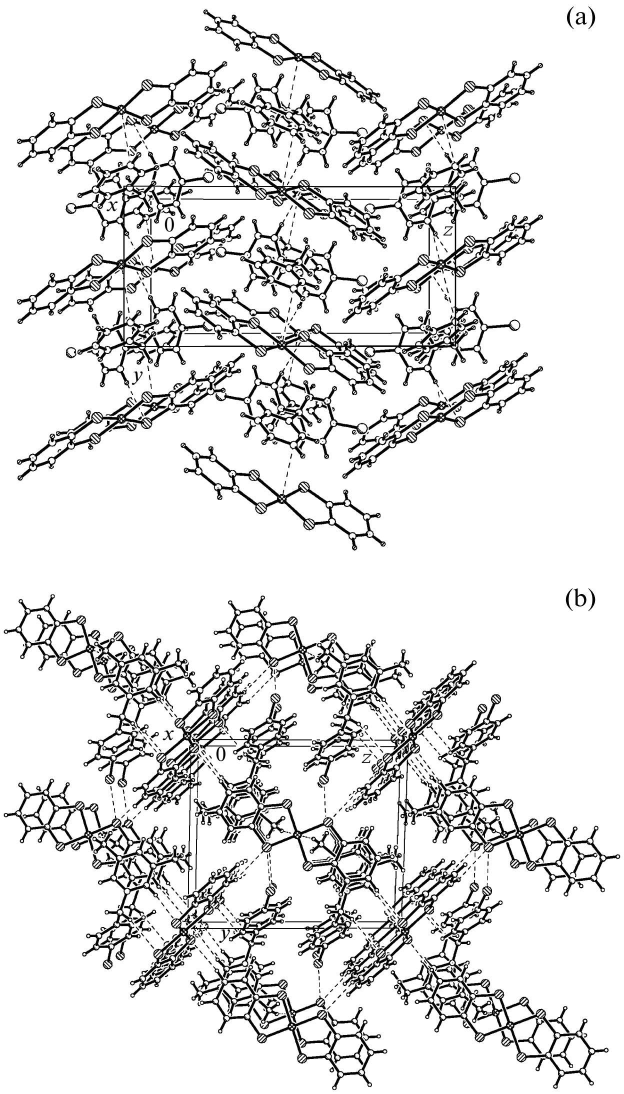

Fig. 3. The packing diagram of **I** (a) and **II** (b) along *x* axis. Hydrogen bonds are indicated by dashed lines.

103 mV) and −321 mV (ΔE = 93 mV), respectively. The redox potentials of the $[Ni(Bdt)_2]$ couples of two complexes lie in the same range as observed for other planar nickel complexes with four sulfur donors [28–31].

In this contribution, we fabricated two new ion-pair complexes containing $[Ni(Bdt)_2]^-$. The central Ni atoms in complexes **I** and **II** are in slightly distorted square-planar coordination environment. The anions are stacked in side-by-side fashion in complex **I**, while two nonequivalent anions are stacked in face-to-face or side-by-side fashion in **II**. The cyclic voltammetric studies show that there are two oxidation peaks for complexes **I** and **II**, which are attributed to the Ni(IV/III) and Ni(III/II) redox couples.

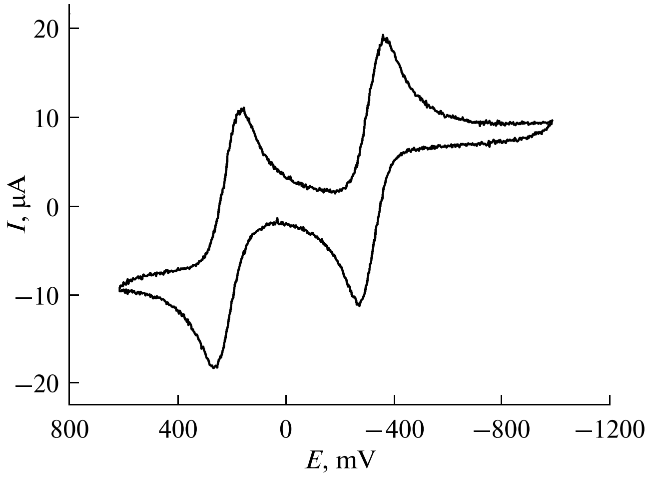

Fig. 4. Cyclic voltammogram of $[IBzPy][Ni(Bdt)_2]$ in CH_3CN.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (no. 20971004), the Natural Science Foundation for Outstanding Scholars of Anhui Province, China (Grant no. 044-J-04011), and the Natural Science Foundation of Education Commission of Anhui Province, China (no. KJ2008B004).

REFERENCES

1. Robertson, N. and Cronin, L., *Coord. Chem. Rev.*, 2002, vol. 227, p. 93.
2. Kato, R., *Chem. Rev.*, 2004, vol. 104, p. 5319.
3. Cassoux, P., *Coord. Chem. Rev.*, 1999, vol. 186, p. 213.
4. Canadell, E., *Coord. Chem. Rev.*, 1999, vol. 186, p. 629.
5. Akutagawa, T. and Nakamura, T., *Coord. Chem. Rev.*, 2000, vol. 198, p. 297.
6. Wen, H.R., Zuo, J.L., Scott, T.A., et al., *Polyhedron*, 2005, vol, 24, p. 671.
7. MacDonald, J.C. and Whitesides, G.M., *Chem. Rev.*, 1994, vol. 94, p. 2383.
8. Aakeroy, C.B. and Seddon, K.R., *Chem. Soc. Rev.*, 1993, vol. 22, p. 397.
9. Tomono, K., Ogawa, K., Sasaki, Y., and Miyamura, K., *Inorg. Chim. Acta*, 2008, vol. 361, p. 269.
10. Kato, M., Sasano, K., Kosuge, C., et al., *Inorg. Chem.*, 1996, vol. 35, p. 116.
11. Munakata, M., Kuroda-Sowa, T., Maekawa, M., et al., *Inorg. Chem.*, 1994, vol. 33, p. 1284.
12. Munakata, M., Dai, J., Maekawa, M., et al., *Chem. Commun.*, 1994, p. 2331.
13. Munakata, M., Kuroda-Sowa, T., Maekawa, M., et al., *Inorg. Chem.*, 1995, vol. 34, p. 2705.
14. Williams, J.M., Wang, H.H., Emge, T.J., et al., *Prog. Inorg. Chem.*, 1987, vol. 35, p. 51.
15. Bryce, M.R., *Chem. Soc. Rev.*, 1991, vol. 20, p. 355.

16. Olk, R.M., Olk, B., Dietzsch, W., et al., *Coord. Chem. Rev.*, 1992, vol. 117, p. 99.
17. Cassoux, P., Valade, L., Kobayashi, H., et al., *Coord. Chem. Rev.*, 1991, vol. 110, p. 115.
18. Ren, X.M., Lu, C.S., Liu, Y.J., et al., *Transition Met. Chem.*, 2001, vol. 26, p. 136.
19. Ren, X.M., Okudera, H., Kremer, R.K., et al., *Inorg. Chem.*, 2004, vol. 43, p. 2569.
20. Ren, X.M., Meng, Q.J., Song, Y., et al., *Inorg. Chem.*, 2002, vol. 41, p. 5686.
21. Xie, J.L., Ren, X.M., He, C., et al., *Chem. Phys. Lett.*, 2003, vol. 369, p. 41.
22. Ren, X.M., Okudera, H., Xie, J.L., and Meng, Q.J., *J. Mol. Struct.*, 2005, vol. 733, p. 119.
23. Bulgarevich, S.B., Bren, D.V., and Movshovic, D.Y., *J. Mol. Struct.*, 1994, vol. 317, p. 147.
24. *SAINT*, Madison (WI, USA): Bruker AXS Inc., 2002.
25. Sheldrick, G.M., *SADABS*, Madison (WI, USA): Bruker AXS Inc., 1997.
26. Sheldrick, G.M., *SHELXS-97*, Madison (WI, USA): Bruker AXS Inc., 1997.
27. Sheldrick, G.M., *SHELXL-97*, Madison (WI, USA): Bruker AXS Inc., 1997.
28. Liu, G.X., Huang, L.F., and Ren, X.M., *Appl. Organomet. Chem.*, 2007, vol. 21, p. 1054.
29. Xie, J.L., Ren, R.M., He, C., et al., *Polyhedron*, 2003, vol. 22, p. 299.
30. Sellmann, D., Fünfgelder, S., Knoch, F., and Moll, M.Z., *Naturforsch., B*, 1991, vol. 46, p. 1601.
31. Sellmann, D., Binder, H., Haüginger, D., et al., *Inorg. Chim. Acta*, 2002, vol. 300–302, p. 82.