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Synthesis and characterization of pyridine N-oxide complexes of manganese, copper and zinc

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Abstract

A series of metal carboxylates containing pyridine N-oxide are prepared via one pot synthesis and solid phase synthesis. The structural variations from metal to metal are observed. In the case of reactions of manganese(II) acetate with pyridine N-oxide in the presence of aromatic carboxylic acids, polymeric complexes with bridging aromatic carboxylate as well as bridging pyridine N-oxide are observed. Whereas, the reaction of copper(II) acetate with pyridine N-oxide in the presence of an aromatic carboxylic acid led to mononuclear or binuclear paddle wheel carboxylate complexes with monodentate pyridine N-oxide. Co-crystal of two neutral complexes having composition $[Cu_2(OBz)_4(MeOH)_2][Cu_2(OBz)_4(pyO)_2]$ (where OBz = benzoate, pyO = pyridine N-oxide) each neutral parts have paddle wheel structure. Solid phase reaction of zinc chloride with sodium benzoate prepared in situ and pyridine N-oxide leads to a tetra-nuclear zinc complex.

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Keywords: Metal-carboxylates; Pyridine N-oxide; Co-ordination polymers; Co-crystals

1. Introduction

Pyridine N-oxide is an important reagent for oxo-transfer reactions [1]. Such reactions are facilitated by transition metal complexes [2]. Many N-oxide complexes have been prepared and studied [3]. The N-oxide containing metal complexes are also of special interest as magnetic material [4]. The nitroxide complexes also form polymeric structures and their magnetic properties [5] and electrochemical properties [6] are studied. Nitroxides can co-ordinate as monodentate and bridging ligand, which complicates structural studies [7]. For example a complex having composition [Co(pyO)Cl₂(H₂O)] (where pyO = pyridine N-oxide) has halogen and also N-oxide bridge in its polymeric structure [3h]. The carboxylate containing nitroxide complexes are known in the literature but they have further structural complicacy as the carboxylate group it self have multiple ways to bind to a metal [4h,5]. Thus, a general approach to synthesize pyridine N-oxide containing metal carboxylate complexes is essential. We have made a series of study to prepare aromatic carboxylate complexes through solution phase and solid phase reactions [8]. We used nitrogen containing ligand in all these studies [8]; here we present preliminary results on the general methodology for synthesis of metal carboxylate complexes containing pyridine Noxide.

2. Experimental

The complexes $[Mn(OBz)_2(pyO)]_n$ **1a**, $[Mn(pNO_2-OBz)_2(pyO)]_n$ **1b**, $[Cu_2(OBz)_4 \cdot (MeOH)_2][Cu_2(OBz)_4 (pyO)_2]$ **2a**, $Cu(pNO_2OBz)_2(pyO)_2]$ **2b** were prepared through solution chemistry. Whereas complex $[Zn_4(OBz)_8 (pyO)_3(H_2O)_2]H_2O$ **3** was prepared by solid phase synthesis. (where $OBz = C_6H_5CO_2$, $pNO_2OBz = 4-NO_2C_6H_4$ CO_2 , and $pyO = C_5H_5NO$)

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3. Typical procedure for synthesis of 1a

To a solution of benzoic acid (2 mmol, 0.242 g) in methanol (20 ml), Mn(OAc)₂ · 4H₂O (1 mmol, 0.245 g) was added and stirred for 10 min to obtain a homogeneous solution. To this reaction mixture pyridine N-oxide (3 mmol, 0.285 g) was added with constant stirring at room temperature. The colour of the solution changes to yellow. A small amount (\approx 2 ml) of water was added to dissolve the precipitate that appeared after addition of pyridine Noxide. Yellow coloured crystals were collected after 3 days and dried in air. Yield of the pure crystalline complex was found to be 27% (crude yield >70%). IR (KBr, cm⁻¹): 1593 (m), 1557 (s), 1477 (w), 1397 (s), 1219 (m), 731 (m). Molar conductance: 129.3 S cm² mol⁻¹ in water and 55.0 S cm² mol⁻¹ in methanol. Magnetic moment μ_{eff} : 5.38 B.M.(RT).

Complexes **1b**, **2a** and **2b** were prepared with similar procedure and crystalline pure products with 21%, 24% and 29% yield, respectively, were obtained. *Complex* **1b**: IR (KBr, cm⁻¹): 1580 (s), 1518 (m), 1471 (w), 1398 (s), 1343 (s), 1208 (m), 1102 (w), 1020 (m), 820 (m), 727 (m). Molar conductance: 124 S cm² mol⁻¹ in water. Magnetic moment μ_{eff} : 5.62 B.M. *Complex* **2a**: IR (KBr, cm⁻¹):

Table 1

The crystal	l parameters	of the	complexes	1a-b,	2a-b	and	3
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3453 (br m), 3067 (m), 1627 (s), 1572 (s), 1470 (w), 1405 (s), 1224 (m), 1020 (m), 1176 (s), 719 (m). Molar conductance: 12.80 S cm² mol⁻¹ in methanol. Magnetic moment, μ_{eff} : 1.93 B.M.(RT). λ_{max} (methanol): 713 nm; $\varepsilon = 350 \text{ M}^{-1} \text{ cm}^{-1}$. Complex **2b**: IR (KBr, cm⁻¹): 1630 (m), 1583 (s), 1514 (s), 1469 (m), 1392 (w), 1340 (s), 1199 (m), 829(m), 723 (m); Magnetic moment, μ_{eff} : 1.91 B.M.(RT). λ_{max} (methanol): 705 nm; $\varepsilon = 349 \text{ M}^{-1} \text{ cm}^{-1}$.

Synthesis of 3: A mixture of benzoic acid (0.242 g, 2 mmol) and potassium hydroxide (0.113 g, 2 mmol) was finely ground in a pastel mortar and heated at 90 °C for 15 min. The mixture was cooled to room temperature. Anhydrous ZnCl₂ (0.136 g, 1 mmol) was added. The mixture was finely ground and heated again at 90 °C for another 15 min. The mixture was cooled to room temperature, transferred to a round bottom flask, and dissolved in a mixture of methanol/toluene (15 ml/5 ml). To this reaction mixture pyridine N-oxide (0.285 g, 3 mmol) was added with continuous stirring. The solution was then allowed to stand. Colourless crystals were collected after 5 days and dried in air. Yield of the crystalline complex was found to be 26%. ¹HNMR (CDCl₃, ppm): 8.41 (s, 6H), 8.08 (s, 16H), 7.48 (br m, 9H), 7.35 (br s, 24H), 4.2 (br s, exchange-

Complexes	1a	1b	2a	2b	3
Formulae	C19H15MnNO5	C19H13MnN3O9	C68 H58 Cu4 N2O20	C ₂₄ H ₁₈ Cu N ₄ O ₁₀	C71 H63 N3O23 Zn4
Molecular weight	392.26	482.26	1477.32	585.96	1587.72
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic	monoclinic
Space group	pbcn	C2/c	$P\overline{1}$	P2(1)/n	C2/c
Temperature (K)	296	296	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
a (Å)	16.5652(14)	25.6908(8)	10.6502(8)	6.6443(4)	25.3108(10)
b (Å)	13.3047(10)	9.7787(3)	10.6939(8)	7.0988(4)	9.6114(3)
<i>c</i> (Å)	7.5755(6)	7.6613(3)	15.4901(11)	25.1865(18)	31.4127(14)
α (°)	90.00	90.00	101.970(4)	90.00	90.00
β (°)	90.00	101.421(2)	105.362(4)	90.402(4)	112.617(4)
γ (°)	90.00	90.00	96.011(4)	90.00	90.00
$V(Å^3)$	1669.6(2)	1886.58(11)	1640.2(2)	1187.93(13)	7054.1(5)
Ζ	4	4	1	2	4
$D_{\text{calc.}}$ (Mg m ⁻³)	1.561	1.698	1.496	1.638	1.495
Absolute coefficient (mm^{-1})	0.822	0.763	1.355	0.988	1.423
Absolute correction	none	none	none	none	none
<i>F</i> (000)	804	980	756	598	3256
Total number of reflections	17272	11049	17 502	11021	26988
Reflections, $I > 2\sigma(I)$	2033	2263	5558	2833	6570
Maximum 2θ (°)	28.37	28.29	25.00	28.36	25.50
Ranges (h, k, l)	$-20 \leqslant h \leqslant 20$	$-34 \leqslant h \leqslant 32$	$-12 \leqslant h \leqslant 11$	$-8 \leqslant h \leqslant 8$	$-30 \leqslant h \leqslant 30$
,	$-14 \leq k \leq 17$	$-12 \leq k \leq 13$	$-12 \leqslant k \leqslant 12$	$-9 \leqslant k \leqslant 9$	$-11 \leq k \leq 11$
	$-10 \leq l \leq 10$	$-10 \leq l \leq 9$	$-18 \leqslant l \leqslant 18$	$-29 \leq l \leq 32$	$-37 \leqslant l \leqslant 38$
Complete to 2θ (%)	97.1	96.4	96.2	95.8	99.8
Refinement method	full-matrix least-	full-matrix least-	full-matrix least-	full-matrix least-	full-matrix least-
	squares on F^2	squares on F^2	squares on F^2	squares on F^2	squares on F^2
Data/restraints/ parameters	2033/0/121	2263/0/148	5558/0/429	2833/0/178	6750/0/473
Goodness-of-fit (F^2)	1.053	1.058	1.049	1.201	1.042
R indices $[I > 2\sigma(I)]$	0.0263	0.0276	0.0299	0.0604	0.0367
R indices (all data)	0.0358	0.0300	0.0406	0.0801	0.0638

able from water), 2.64 (br s, exchangeable from water). IR (KBr, cm^{-1}): 3378 (br s), 1595 (m), 1559 (s), 1475 (m) 1392 (s), 1218 (m), 1023 (m), 829 (m), 731 (m).

3.1. Crystallography

The X-ray diffraction data were collected at 296 K with Mo K α radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with graphite monochromator. The SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All the non-H atoms were refined in the anisotropic approximation. The crystal-lographic parameters of the complexes are given in Table 1.

4. Results and discussion

The reaction of pyridine N-oxide along with aromatic carboxylic acid with metal acetates such as manganese(II) acetate and copper(II) acetate leads to pyridine N-oxide complexes. However, the formation of the type of pyridine N-oxide complexes varies with metal and carboxylic acid under consideration. The reaction of pyridine N-oxide and aromatic carboxylic acid with manganese(II) acetate tetrahydrate under ambient condition is illustrated in Scheme 1. Similar reaction also proceeds smoothly with other acids such as 4-chlorobenzoic acid and 4-nitrobenzoic acid. In each case co-ordination polymers are formed by bridging carboxylate and N-oxide. The crystal structures of the polymeric compounds are determined and two structures are shown in Figs. 1b and c. The complexes have six co-ordination geometry around the manganese ions. The geometry around the manganese (II) in complex 1a is shown in Fig. 1a. The repeated units in the polymeric manganese complexes can be compared with dinuclear aqua bridged metal carboxylate complexes [8a,8b,8j]. In aqua and carboxylato bridged manganese(II) complexes the Mn...Mn separation [8j] are in the range of 3.65-3.74 Å. The Mn ···· Mn separation in the one-dimensional polymers 1a and 1b are 3.79 Å, 3.83 Å, respectively. This shows that pyridine N-oxide bridged complex has slightly



Fig. 1. (a) The co-ordination environment around manganese in complex **1a**, (b) co-ordination polymer **1a**, (c) co-ordination polymer **1b**.

higher Mn · · · Mn separation than the aqua bridged dinuclear manganese carboxylate complexes. At room temperature the two complexes **1a** and **1b**, show relatively low magnetic moments, e.g. **1a** has 5.38 B.M. and **1b** has 5.62 B.M. The calculated spin only magnetic moment for a d⁵ system is 5.92 B.M. Thus, there is magnetic interaction/s between the manganese ions in the lattice which reduces the magnetic moment from the expected value. The compound **1a** is non-ionic in methanol and has molar conductance 55 S cm² mol⁻¹ whereas in water it shows ionization and has molar conductance 124 S cm² mol⁻¹. The compound **1b** is not soluble in methanol and its molar conductance was recorded in water and found to be 125 S cm² mol⁻¹, which suggests that in water it ionizes.

In contrast to these results the copper(II) pyridine Noxide complex has paddle wheel type structure which was



When $Ar = C_6H_5$ -(**1a**) and $4-NO_2-C_6H_4$ -(**1b**)

obtained when benzoic acid along with pyridine N-oxide was reacted with copper(II) acetate. This reaction led to the formation of very interesting co-crystals of two paddle wheel molecules. Recently, we have reported co-crystals that can arise from self-assembling of two or more neutral inorganic complexes [8c,8d,8e]. These are generally held in the lattices by weak interactions, such as C-H···O, C-H··· π interactions. The co-crystal **2a** is also not an exception to this. The two co-crystals are held together by C15-H···O8' (d_{H-A} 3.22 Å and \angle D-H···A 106.86°) and



Fig. 2. Structure of (a) 2a and (b) 2b.

O3–H···O7' (d_{H-A} 3.17 Å and $\angle D$ –H···A 166.91°) interactions. The crystal structure of the compound is shown in Fig. 2a. The co-crystals are non-ionic in methanol and have molar conductance value 13 S cm² mol⁻¹. The co-crystal **2a** shows magnetic moment 1.93 B.M. at room temperature. This shows that there is no significant interaction among the copper(II) ions in the co-crystal. The compound has a broad absorption in visible spectra at 713 nm which is attributed to E–T₂ transition. The two Cu ···Cu separation in the two neutral paddle wheel are 2.616 Å and 2.620 Å, respectively, which is slightly longer than the distance observed in copper(II) acetate (2.614 Å) but comparable to copper carboxylate complexes with aromatic carboxylato groups [8h].

The reaction of 4-nitro-benzoic acid and pyridine Noxide with copper(II) acetate led to the formation of mono-nuclear complex **2b** having two molecules of pyridine N-oxide co-ordinated to copper(II) 4-nitrobenzoate (Scheme 2). From the crystal structure it is clear that the complex has six co-ordination geometry. The compound is highly symmetric and has Cu1–O1, Cu1–O2 and Cu1– O5 bond distances as 1.95 Å, 2.66 Å and 1.98 Å, respectively. Thus, the two oxygen atoms occupying axial positions have longer Cu-O bond distances than the other two and suggest a strong Jahn–Teller distortion in the complex. The compound has very broad and distorted absorbance at 705 nm due to $E \rightarrow T_2$ transition which supports a distorted six co-ordination environment in solution.

The zinc(II)acetate on reaction with benzoic acid and pyridine N-oxide gave a tetra-nuclear complex having composition $[Zn_4(OBz)_8(pyO)_3(H_2O)_2]H_2O$ (3). The reaction is shown in Scheme 3. The complex has six co-ordination around all the four zinc ions and the repeated unit in a unit cell of the complex is illustrated in Fig. 3a. Each unit has three bridging pyridine N-oxide and six bridging carboxylates. There are two monodentate carboxylates attached one



Scheme 2.







Fig. 3. Structure of the (a) repeated unit in the tetra-nuclear zinc complex 3, (b) the complex 3.

each to the two terminal zinc ions of the tetra-nuclear complex. The structure of the complex is shown in Fig. 3b. In solid state the complex, self-assembles through hydrogen bond interactions between the aqua ligands, water of crystallization along with the carbonyl group of the mono-dentate carboxylate group. The complex shows absorbance at 1595 cm⁻¹ and at 1559 cm⁻¹ due to terminal and bridging carboxylate groups. The terminal monodentate carboxylate absorption is at lower frequency due to hydrogen bond-

ing with the co-ordinated water molecule and also with the water of crystallization. The complex has some similarity to the polynuclear complexes of carboxylate complexes of cobalt and few other metals [9] in which the role of pyridine N-oxide is played by a carboxylate group which has chelating as well as bridging co-ordination mode.

In these complexes the N–O stretching absorptions are prominent in IR spectroscopy. The bridging N–O absorption in the complex **1a**, **1b** and **3** occurs at 1219 cm⁻¹, 1208 cm⁻¹ and 1218 cm⁻¹ whereas in the mono-dentate N–O absorption in **2a** and **2b** occurs at 1224 cm⁻¹ and 1199 cm⁻¹.

In conclusion, metal carboxylate complexes containing pyridine N-oxide can easily be prepared by ligand exchange reactions of metal acetates in the presence of an aromatic carboxylic acid. The structural diversity of the complexes and formation of co-ordination polymer with uniform chain under ambient condition provides wide scope for synthesis of varieties of new class of mixed ligand complexes.

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Appendix A. Supplementary data

CCDC 650977, 650978, 650979, 650980, 650982 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.10.029.

References

[1] (a) K.M. Sung, R.H. Holm, J. Am. Chem. Soc. 123 (2001) 1931;

(b) E.W. Harlan, J.M. Berg, R.H. Holm, J. Am. Chem. Soc. 108 (1986) 6992;

(c) N. Ueyama, N. Yoshinaga, A. Nakamura, J. Chem. Soc., Dalton Trans. (1990) 387;

- (d) D. Chatterjee, J. Mol. Catal. A: Chem. 150 (1999) 49;
- (e) J.H. Espenson, Adv. Inorg. Chem. 54 (2003) 157.
- [2] (a) J. Jacob, I.A. Guzei, J.H. Espenson, Inorg. Chem. 38 (1999) 1040;
 (b) N. Ueyama, N. Yoshinaga, A. Nakamura, J. Chem. Soc., Dalton Trans. (1990) 387;

(c) Y. Sun, N. Tang, J. Mol. Catal. A: Chem. 255 (2006) 171;

(d) A. Bakac, V. Butkovic, J.H. Espenson, J. Lovric, M. Orhanovic, Inorg. Chem. 35 (1996) 5168;

- (e) S.M. Mullins, R.G. Bergman, J. Arnold, Organometallics 18 (1999) 4465. [3] (a) W.E. Purcell, Coord. Chem. Rev. 28 (1989) 2312;
 - (b) N.M. Karayannis, Coord. Chem. Rev. 11 (1973) 93;
 - (c) A.B.P. Lever, J. Chem. Soc. (1962) 5262;

(d) L.C. Nathan, J.E. Armstrong, R.O. Ragsdale, Inorg. Chim. Acta 35 (1979) 293;

- (e) M. Kotowski, R. Marcec, V. Butkovic, A. Bakac, M. Orhanovic, Eur. J. Inorg. Chem. 17 (2006) 2894;
- (f) S.E. Denmark, F. Yu, Tetrahedron: Asymmetry 17 (2006) 687;
- (g) J.M. Shi, J.N. Chen, C.J. Wu, L.D. Liu, Acta Crystallogr., Sect. E
- (2005) M2621;
- (h) M. Nieuwenhuyzen, W.T. Robinson, C.J. Wilkins, Polyhedron 9 (1990) 2315.
- [4] (a) H. Kanno, T. Yano, K. Sato, S. Utsuno, J. Fujita, Bull. Chem. Soc. Jpn. 70 (1997) 1085;

(b) M. Boca, M. Izakovic, G. Kickelbick, M. Valko, F. Renz, H. Fuess, K. Matuzsna, Polyhedron 24 (2005) 913;

- (c) P. Baran, R. Boca, M. Breza, H. Elias, H. Fuess, V. Jorik, R. Klement, I. Svoboda, Polyhedron 21 (2002) 1561;
- (d) R.E. Del Sesto, A.M. Arif, J.S. Miller, Inorg. Chem. 39 (2000) 4894;

(e) G. Poneti, K. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer, D. Gatteschi, Chem. Commun. (2007) 1807;

(f) Q. Yu, L-G. Zhu, H-D. Bian, J-H. Deng, X-G. Bao, H. Liang, Inorg. Chem. Commun. 10 (2007) 437;

(g) A.B. Blake, E. Sinn, M. Yavaria, K.S. Murray, Inorg. Chim. Acta 229 (1995) 281;

(h) L.S. Gelfand, L.L. Pytlewski, A.N. Speca, C.M. Mikulski, N.M. Karayannis, J. Inorg. Nucl. Chem. 42 (1980) 209.

- [5] (a) D. Luneau, P. Rey, J. Laugier, P. Fries, A. Caneschi, D. Gatteschi, R. Sessoli, J. Am. Chem. Soc. 113 (1991) 1245;
 (b) Y. Karaki, R. Masutomi, H. Ishimoto, T. Asano, Y. Ajiro, Phys. B: Condens. Matter 329–333 (2003) 1002.
- [6] S. Hotchandani, U. Ozdemir, S.I. Allakhverdiev, N. Karacan, V.V. limov, P.V. Kamat, R. Carpentier, Bioelectrochemistry 51 (2000) 175.
- [7] (a) J.R. Bower, G.W. Hopkins, G.P.A. Yap, K.A. Wheeler, Cryst. Growth Des. (2005) 5727;
 (b) S.E. Edison, J.A.K. Bauer, M.J. Baldwin, Acta Crystallogr., Sect. E
- 60 (2004) M1930.
- [8] (a) A. Karmakar, R.J. Sarma, J.B. Baruah, Eur. J. Inorg. Chem. (2007) 643;

(b) A. Karmakar, R.J. Sarma, J.B. Baruah, Eur. J. Inorg. Chem. (2006) 4673;

(c) N. Barooah, A. Karmakar, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 1251;

(d) A. Karmakar, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 1169;

- (e) K. Deka, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 931;
- (f) N. Barooah, R.J. Sarma, J.B. Baruah, Eur. J. Inorg. Chem. (2006) 2942;
- (g) A. Karmakar, K. Deka, R.J. Sarma, J.B. Baruah, Inorg. Chem. Commun. 9 (2006) 836;
- (h) K. Deka, N. Barooah, R.J. Sarma, J.B. Baruah, J. Mol. Struct. 827 (2007) 44;
- (i) A. Karmakar, R.J. Sarma, J.B. Baruah, Polyhedron 26 (2007) 1347;
 (j) A. Karmakar, K. Bania, A. Baruah, J.B. Baruah Inorg. Chem.
- Commun., dx.doi.org/ 10.1016/j.inoche.2007.04.026.
- [9] K.S. Gavrilenko, S.V. Punin, O. Cador, S. Golhen, L. Quahab, V.V. Pavlishchuk, J. Am. Chem. Soc. 127 (2005) 12246.