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Salts with the $[NiBr_3(L)]^-$ complex anion (L = 1-methylimidazole, 1-methylbenzimidazole, quinoline, and triphenylphosphane) and low melting points: A comparative study

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Dedicated on the Occasion of the 100th Anniversary of the 1913 Noble Prize in Chemistry to Alfred Werner.

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ABSTRACT

Four new salts with low melting points of the general formula (EMIm)$[NiBr_3(L)]$ (EMIm = 1-ethyl-3-methyl-imidazolium) with L = *N*-methylimidazole (NMIm), *N*-methylbenzimidazole (NMBIm), quinoline (quin), and triphenylphosphane (PPh_3) were prepared and characterized by means of elemental analysis, IR, NMR, and UV–vis spectroscopy. Magnetic properties were deduced from NMR data using the EVANS method. All four compounds are paramagnetic with magnetic moments close to the spin-only values of the tetrahedrally coordinated Ni(II) ion. Molecular and crystal structures were obtained by single crystal X-ray diffraction investigations. Melting points are determined to have values between 110 °C, (EMIm)$[NiBr_3(NMIm)]$ and 168 °C, (EMIm)$[NiBr_3(PPh_3)]$. They exceed the maximum temperature required to call them “Ionic Liquids”. Decomposition has been found to occur above 200 °C and to depend largely on the type of organic ligand coordinated to Ni(II).

1. Introduction

Solids with low melting points have found many applications as reaction media for the production of a wide range of materials. Especially the so-called Ionic Liquids have been in the focus of interest for their unique properties for more than two decades. Characteristics are melting points below 100 °C, wide temperature ranges wherein the salts are liquid, low vapor pressures, and high electric conductivities [1], to name just a few. Paramagnetic complex anions incorporated in Ionic Liquids result in substances with the intriguing combination of properties of being both liquid and responding to magnetic fields [2]. The work of Hayashi et al. on $[FeCl_4]^-$ containing Ionic Liquids [2] boosted research on transition metal containing Ionic Liquids, because of numerous possible applications, like transport and materials separation [2e], catalysis [2f] or field dependent absorption [2g], to name a few. An example of a similar paramagnetic ion is that of the general formula $[MX_3(\mathrm{quin})]^-$ (M = 3d-metal; X = Cl, Br, I; quin = quinoline) which is known for Mn(II) [3], Fe(II) [4], Co(II) [5], Ni(II) [2c,6], Cu(II) [7], and Zn(II) [8]. Preparative investigations were conducted in our laboratories to find cation combinations with such anions with low melting points. Recently, we have investigated a series of Ionic Liquids containing the $[CoBr_3(\mathrm{quin})]^-$ anion [9]. To get a better understanding of the relation between thermal properties and solid state characteristics the neutral ligand in this type of anion is varied.

In this contribution we report on the syntheses, properties, and structures of a series of (EMIm)$[NiBr_3(L)]$ salts (EMIm = 1-ethyl-3-methyl-imidazolium) with L = *N*-methylimidazole (NMIm), *N*-methylbenzimidazole (NMBIm), quinoline (quin), and triphenylphospane (PPh_3)).

2. Experimental

2.1. Materials and methods

N-Methylimidazole, quinoline, benzimidazole, iodomethane and anhydrous $NiBr_2$ were purchased from Sigma–Aldrich (>99%) and used as received. *N*-Methyl-benzimidazole was synthesized according to a known literature method [10]: Benzimidazole (25.0 g, 211.6 mmol) is added in one portion to 100 mL of a stirred ice-cold 50% aqueous NaOH solution. Iodomethane (33.0 g, 232.8 mmol) is added dropwise under vigorous stirring to the clear benzimidazole solution at ambient temperature. After 1 h the solution is extracted three times with 100 mL portions of chloroform. The combined organic phases are dried with Na_2SO_4 and the solvent is removed under reduced pressure. The residue is distilled

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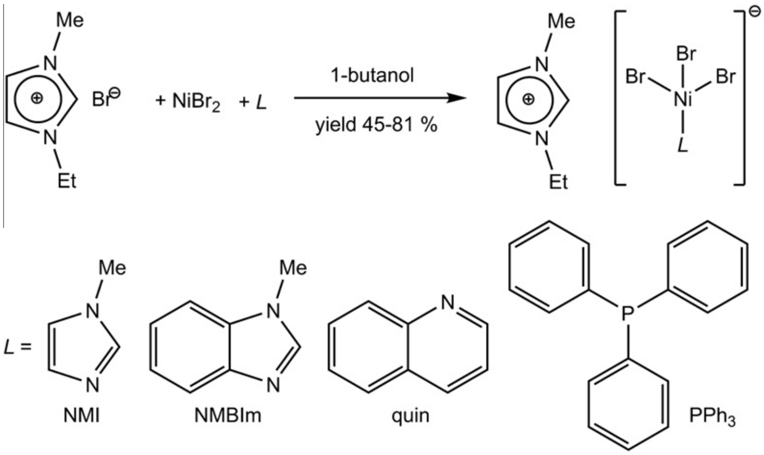
Table 1
Crystal data and structure refinement parameters for (EMIm)[NiBr$_3$(L)], with L = NMIm, NMBIm, quin, and PPh$_3$.

L	NMIm	NMBIm	Quin	PPh$_3$
Formula	$C_{10}H_{17}Br_3N_4Ni$	$C_{14}H_{19}Br_3N_4Ni$	$C_{15}H_{18}Br_3N_3Ni$	$C_{24}H_{26}Br_3N_2NiP$
Formula weight	491.72	541.77	538.76	671.88
T (K)	173(2)	173(2)	173(2)	173(2)
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1$/n (No. 14)	$P2_1$/c (No. 14)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)
Z	4	4	2	2
Unit cell dimensions				
a (Å)	7.742(2)	13.8876(4)	7.4845(5)	10.4387(2)
b (Å)	14.506(3)	10.4570(3)	8.1975(6)	11.0013(2)
c (Å)	14.843(3)	12.9338(3)	15.204(1)	13.8378(2)
α (°)	90	90	88.331(5)	79.131(1)
β (°)	92.01(3)	92.165(1)	85.297(5)	71.119(1)
V (Å^3)	1665.9(6)	1876.94(9)	913.2(1)	1331.83(4)
$\rho_{calc.}$ (g·cm^{-3})	1.961	1.917	1.959	1.675
μ (mm^{-1})	8.349	7.421	7.624	5.303
λ (Å)	0.71073	0.71073	0.71073	0.71073
No. parameters	164	200	200	290
Goodness-of-fit (GOF) on F^2	1.021	1.028	1.052	1.039
Final R indices $[I > 2\sigma(I)]$[a,b]	$R1$ = 0.0381, $wR2$ = 0.0663	$R1$ = 0.0223, $wR2$ = 0.0488	$R1$ = 0.0326, $R2$ = 0.0714	$R1$ = 0.0327, $wR2$ = 0.0719
Weighting A/B[c]	0.0225/1.1862	0.0220/1.0026	0.0339/0.6411	0.0335/0.4157

[a] $R1 = \sum ||F_o| - |F_c||/\sum |F_c|$.

[b] $wR2 = \sqrt{\left[\sum\{w(F_o^2 - F_c^2)^2\}/\sum\{w(F_o^2)^2\}\right]}$.

[c] $w = 1/[\sigma_2(F_0^2) + (A \cdot P)^2 + B \cdot P]$; $P = (F_0^2 + 2F_c^2)/3$.



Scheme 1. Reaction sequence for the synthesis of (EMIm)[NiBr$_3$(L)].

in vacuo, yielding *N*-methyl-benzimidazole as a colorless liquid, which solidifies upon cooling. Yield: 21.0 g (75%), mp. 61 °C. Elemental anal. % (calc. for $C_8H_8N_2$): C, 72.50 (72.70); H, 6.19 (6.10); N, 21.18 (21.20).

2.2. General synthesis of (EMIm)[NiBr$_3$(L)] (L = NMIm, NMBIm, quin, PPh$_3$)

1-Ethyl-3-methylimidazolium bromide ((EMIm)Br, 0.9 g, 4.7 mmol) and appropriate ligand L (4.7 mmol; PPh$_3$: 1.2 g, quin: 0.6 g, NMIm: 0.4 g, NMBIm: 0.6 g) are dissolved in 25 mL of hot 1-butanol and added to a vigorously stirred boiling suspension of NiBr$_2$ (1.0 g, 4.6 mmol) in 25 mL of the same solvent. The resulting mixture turns dark blue immediately and the desired product precipitates in form of crystals upon storing the solution at 0 °C overnight. The precipitate is filtered off, washed with diethyl ether and finally dried *in vacuo* at ambient temperature.

(EMIm)[NiBr$_3$(PPh$_3$)]: Yield: 2.5 g, 81%, mp. 168 °C. Elemental anal. % (calc. for $C_{24}H_{26}Br_3N_2NiP$): C, 42.59 (42.90); H, 3.89 (3.90); N, 4.26 (4.17). UV–vis (λ_{max}/nm in acetonitrile, 25 °C): 378 (~390) , 640 (~685). IR (ν_{max}/cm^{-1}): 3144w, 3105w, 3084w, 3053w, 2978w, 2932w, 1584vw, 1568m, 1481m, 1462w, 1435s, 1387w, 1353vw, 1336w, 1315w, 1291w, 1267vw, 1247vw, 1185w, 1167s, 1120w, 1097s, 1073w, 1028w, 995w, 959vw, 932vw, 921vw, 837m, 795w, 756s, 745s, 709m, 693s, 647m, 617s, 594w. Magnetic data: $\mu_{eff}/\mu_B = 3.76$ (T = 25 °C, $c = 2.13 \cdot 10^{-2}$ mol/L, ν_0 = 300 MHz, $\chi_{mol} = 5.93 \cdot 10^{-3}$).

(EMIm)[NiBr$_3$(quin)]: Yield: 1.5 g, 61%, mp. 124 °C. Elemental anal. % (calc. for $C_{15}H_{18}Br_3N_3Ni$): C, 33.47 (33.44); H, 3.37 (3.37); N, 7.67 (7.80). UV–vis (λ_{max}/nm in acetonitrile, 25 °C): 372, 620, 649, 700. IR (ν_{max}/cm^{-1}): 3144w, 3106w, 3080m, 3016vw, 2980w, 2952vw, 2882vw, 2828vw, 1622w, 1593w, 1583vw, 1570m, 1509s, 1455w, 1438w, 1397w, 1377 m, 1342w, 1311m, 1281vw, 1258w, 1234w, 1200w, 1165s, 1127w, 1097vw, 1089w, 1057w, 1026w, 991w, 957m, 866w, 848m, 813s, 779s, 754s, 733s, 708w, 645vw, 636 m, 619s, 529w. Magnetic data: $\mu_{eff}/\mu_B = 3.76$ (T = 25 °C, $c = 2.83 \cdot 10^{-2}$ mol/L, ν_0 = 300 MHz, $\chi_{mol} = 5.92 \cdot 10^{-3}$).