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Novel complexes of 1-(2-hydroxyethyl)-2-methyl-5-nitroimidazole with metal acetates and arylchalcogenylacetates

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Experimental

NMR spectra were recorded on a Bruker DPX 400 spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{15}N, 40.5 MHz, ref. $MeNO_2$) with HMDS as an internal standard in D_2O or CD_3OD. IR spectra were recorded on a Bruker IFS-25 spectrophotometer in KBr. Metronidazole (**MA**), 99.8% was purchased from Aldrich. Metal acetates and arylchalcogenylacetates of metals were prepared as described.[1]

For MA: yield 92%, colourless powder, mp 160-163 ^{o}C. Poorly soluble in alcohol, insoluble in H_2O. IR (KBr, ν/cm^{-1}): 1368 ν (NO_2); 1535 ν (NO_2); 3220 ν (OH). ^{1}H NMR (CD_3OD) δ: 7.90 (s, 1H, H^4); 4.49 (t, 2H, NCH_2); 3.86 (t, 2H, OCH_2); 2.54 (s, 3H, Me). ^{13}C NMR (CD_3OD) δ: 151.84 (C^5); 138.83 (C^2); 131.31 (C^4); 60.40 (OCH_2); 47.76 (NCH_2); 13.04 (Me). ^{15}N NMR (CD_3OD) δ: -131.5 (δ^{15}N^3); -217.0 (δ^{15}N^1); δ^{15}N for NO_2 not registered..

For **1**: yield 99 %, colourless powder, mp 54-55 ^{o}C. IR (KBr, ν/cm^{-1}): 1368 (NO_2), 1535 (NO_2), 1610 (C=O); 2600-3000 (N^+H); 3220 (OH). ^{1}H NMR (CD_3OD) δ: 8.50 (s, 1H, H^4); 4.65 (t, 2H, NCH_2); 3.90 (t, 2H, OCH_2); 2.70 (s, 3H, Me). ^{13}C NMR (CD_3OD) δ: 160.87 (q, C=O); 152.02 (C^5); 139.97 (C^2); 128.32 (C^4); 117.43 (q, CF_3); 61.25 (OCH_2); 50.45 (NCH_2); 13.44 (Me). ^{15}N NMR (CD_3OD) δ: -177.6 (N^3); -217.5 (δ^{15}N^1). Found (%): C, 33.99; H, 3.82; N, 14.30. Calc. for $C_8H_{10}F_3N_3O_5$ (%): C, 33.69; H, 3.53; N, 14.73.

For **3**: yield 98%, colourless powder, mp 77-78 ^{o}C. IR (KBr, ν/cm^{-1}): 1370 ν(NO_2), 1535 ν(NO_2), 1600 (C=O), 3245 (OH). ^{1}H NMR (CD_3OD) δ: 8.01 (s, 2H, H^4); 4.52 (t,

4H, NCH_2); 3.86 (t, 4H, OCH_2); 2.59 (s, 6H, Me), 2.00 (s, 6H, CH_3COO). ^{13}C NMR (CD_3OD) δ: 181.24 (C=O); 153.46 (C^5), 139.86 (C^2), 131.74 (C^4), 61.42 (OCH_2); 49.99 (NCH_2); 22.38 ($\underline{C}H_3COO$), 14.10 (Me). ^{15}N NMR (CD_3OD) δ: -149.0 (N^3); -216.3 ($\delta^{15}N^1$). Found (%): C, 36.84; H, 4.89; N, 16.18; Zn 12.72. Calc. for $C_{16}H_{24}N_6O_{10}Zn$ (%): C, 36.55; H, 4.60; N, 15.98; Zn 12.43.

For **4**: yield 99 %, light green powder, mp 130-132 ^oC. IR (KBr, ν/cm^{-1}): 1368 (NO_2), 1535 (NO_2), 1620 (C=O), 3220 (OH). ^1H, ^{13}C, $^{15}N^3$ NMR failed to record. Found (%): C, 34.79; H, 4.05; N, 12.30; Ni 17.12. Calc. for $C_{10}H_{15}N_3O_7Ni$ (%): C, 34.51; H, 4.34; N, 12.07; Ni, 16.86.

For **6**: yield 98%, colourless powder, mp 152 ^oC. IR (KBr, ν/cm^{-1}): 1367 (NO_2), 1534 (NO_2), 1599 (C=O), 3219 (OH). ^1H NMR (CD_3OD) δ: 8.00 (s, 1H, H^4); 7.25-7.20 (m, 8H, C_6H_4); 4.58 (s, 4H, $OOCCH_2$); 4.44 (t, 2H, NCH_2); 3.82 (t, 2H, OCH_2); 2.53 (s, 3H, CH_3). Found (%): C, 41.15; H, 3.56; N, 6.31; Zn 10.49. Calc. for $C_{22}H_{21}N_3O_7Cl_2S_2Zn$ (%): C, 41.29; H, 3.30; N, 6.56; Zn, 10.21.

For **7:** yield 99%, colourless powder, mp 157-158 ^oC. Not soluble in alcohol. IR (KBr, ν/cm^{-1}): 1368 (NO_2), 1535 (NO_2), 1611 (C=O), 3220 (OH). ^1H NMR (D_2O, 80^o C) δ: 8.50 (s, 2H, H^4); 7.67-7.32 (m, 8H, C_6H_4); 5.02 (s, 4H, $OOCCH_2$); 4.93 (t, 4H, NCH_2); 4.34 (t, 4H, OCH_2); 2.95 (s, 6H, CH_3); 2.71 (s, 6H, $C\underline{H}_3C_6H_4$). ^{13}C NMR (D_2O, 25^o C) δ: 188.40 (C=O); 153.00 (C^5); 147.17 (C_6H_4); 139.76 (C^2); 130.95 (C^4); 130.85-111.52 (C_6H_4); 68.00 ($OOC\underline{C}H_2$); 60.10 (OCH_2); 48.09 (NCH_2); 15.46 ($\underline{C}H_3C_6H_4$), 13.30 (Me). Found (%): C, 50.84; H, 5.37; N, 11.71; Ca 5.89. Calc. for $C_{30}H_{36}N_6O_{12}Ca$ (%): C, 50.55; H, 5.09; N, 11.79; Ca, 5.62.

For **8**: yield 98%, pink powder, mp 95-97 ^oC. IR (KBr, ν/cm^{-1}): 1367 (NO_2), 1536 (NO_2), 1600 (C=O), 3220 (OH). ^1H, ^{13}C, $^{15}N^3$ NMR failed to record. Found (%): C, 46.26; H, 4.68; N, 11.21; Mn 7.80. Calc. for $C_{28}H_{32}N_6O_{14}Mn$ (%): C, 45.97; H, 4.40; N, 11.48; Mn, 7.51.

For **9:** yield 99%, colourless powder, mp 119-120 ^oC. IR (KBr, ν/cm^{-1}): 1368 (NO_2), 1535 (NO_2), 1624 (C=O), 3220 (OH). ^1H NMR (CD_3OD) δ: 7.95 (s, 4H, H^4); 7.08-6.76 (m, 8H, C_6H_4); 4.55 (s, 4H, $OOCCH_2$); 4.47 (t, 8H, NCH_2); 3.85 (t, 8H, OCH_2); 2.52 (s, 12H, CH_3); 2.23 (c, 6H, $C\underline{H}_3C_6H_4$). ^{13}C NMR (CD_3OD) δ: 177.00 (C=O); 153.03 (C^5);

147.07, 139.06 (C^2); 131.15 (C^4); 131.01-111.06 (C_6H_4); 67.08 ($OOC\underline{C}H_2$); 61.06 (OCH_2); 50.06 (NCH_2); 16.08 $\underline{C}H_3C_6H_4$), 14.07 (CH_3). ^{15}N NMR (CD_3OD) δ: -139.5 (N^3); -217.8 ($\delta^{15}N^1$). Found (%): C, 47.00 H, 4.78; N, 15.25; Zn 6.34. Calc. for $C_{42}H_{54}N_{12}O_{18}Zn$ (%): C, 46.70; H, 5.03; N, 15.55; Zn, 6.05.

References

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