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ABSTRACT

This research was focussed on Co(II) and Fe(II) complexes, designed to be thermally stable, magnetic with spin-crossover (SCO) behaviour, and exhibit mesomorphisms. A total of 14 mononuclear octahedral complexes of general formula $[M(L^n)_2]X_2$, where $M = \text{Co(II)}, \text{Fe(II)}$, $L^n = \text{Schiff bases formed from the condensation reaction between 2,6-pyridinedicarboxaldehyde and linear chain 1-aminoalkanes } (C_nH_{2n+1}NH_2, n = 6, 8, 10, 12, 14, 16)$, and $X = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^-$, were successfully prepared by the one-pot method.

The structures of these complexes were deduced from CHN microanalyses, ESI-mass spectrometry, FTIR spectroscopy and UV-vis spectroscopy. Their magnetic properties were determined at room temperature by the Gouy method, and for selected complexes at variable temperatures using the SQUID magnetometer. Finally their thermal and mesomorphic properties by thermogravimetry (TGA), differential scanning calorimetry (DSC), and polarising optical microscopy (POM) were measured. Two complexes, specifically $[\text{Co}(L^{12})_2](\text{BF}_4)_2$ and $[\text{Fe}(L^6)_2](\text{ClO}_4)_2$, were single crystals.

At room temperature, all Co(II) complexes with C_6-C_{10} alkyl chain were a mixture of low spin (LS) and high spin (HS), while complexes with $C_{12}-C_{16}$ alkyl chain were mainly HS. The HS Co(II) complexes showed normal SCO behaviour in the solid state with $T_{1/2}$ at almost room temperature. Complexes with larger anions (ClO_4^- and PF_6^-) contained lower percentages of HS Co(II).

All Fe(II) complexes were mainly LS (89 – 99%) at room temperature. There were no correlation between anionic sizes and percentage of LS in these complexes.

The decomposition temperatures of these complexes were in the range of 97 °C – 246 °C. Complexes with BF_4^- ion and long alkyl chains ($C_{12}-C_{16}$) were mesomorphic with columnar (*Col*) mesophase.

ABSTRAK

Penyelidikan ini berfokuskan kompleks Co(II) dan Fe(II), yang direka bentuk supaya stabil secara terma, magnetik dengan kelakuan pindahan spin (SCO), dan menunjukkan mesomorfisme. Sejumlah 14 kompleks mononukleus oktahedron dengan formula umum $[M(L^n)_2]X_2$, iaitu $M = \text{Co(II)}, \text{Fe(II)}$, $L^n = \text{bes Schiff yang terbentuk daripada tindak balas kondensasi antara 2,6-piridinadikarboksaldehid dan 1-aminoalkana rantai linear}$ ($C_nH_{2n+1}NH_2$, $n = 6, 8, 10, 12, 14, 16$), dan $X = \text{BF}_4^-, \text{ClO}_4^-, \text{PF}_6^-$, berjaya disediakan melalui kaedah satu pot.

Struktur kompleks dideduksikan daripada mikroanalisis CHN, spektrometri ESI-jisim, spektroskopi FTIR dan spektroskopi UV-vis, sifat magnet ditentukan pada suhu bilik melalui kaedah Gouy, dan untuk kompleks terpilih pada suhu pelbagai menggunakan magnetometer SQUID, dan akhir sekali sifat terma dan mesomorfik melalui termogravimetri (TGA), kalorimeter pembeza imbasan (DSC), dan mikroskopi pengutuban optik (POM). Dua kompleks, iaitu $[\text{Co}(L^{12})_2](\text{BF}_4)_2$ dan $[\text{Fe}(L^6)_2](\text{ClO}_4)_2$, adalah hablur tunggal.

Pada suhu bilik, semua kompleks Co(II) dengan rantai alkil C_6-C_{10} adalah satu campuran spin rendah (LS) dan spin tinggi (HS), manakala kompleks dengan rantai alkil $C_{12}-C_{16}$ adalah HS. Kompleks Co(II) HS menunjukkan kelakuan SCO pada keadaan pepejal dengan $T_{1/2}$ pada hampir suhu bilik. Kompleks dengan anion yang lebih besar (ClO_4^- dan PF_6^-) mengandungi peratus Co(II) HS yang lebih rendah.

Semua kompleks Fe(II) adalah kebanyakannya LS (89 – 99%) pada suhu bilik. Tidak terdapat hubungkait antara saiz anion dengan peratus LS dalam semua kompleks ini.

Suhu penguraian kompleks ini adalah dalam julat $97\text{ }^\circ\text{C} - 246\text{ }^\circ\text{C}$. Kompleks dengan ion BF_4^- dan rantai alkil panjang ($C_{12}-C_{16}$) adalah mesomorfik dengan mesofasa turus (*Col*).

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