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Self-assembled Co(II) molecular squares incorporating the bridging ligand 4,7-phenanthrolino-5,6:5′,6′-pyrazine†

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Three high-spin tetranuclear cobalt(II) complexes have been prepared with the bridging ligand 4,7-phenanthrolino-5,6:5′,6′-pyrazine (ppz) through metal-ion directed self-assembly. The complexes differ by the incorporation of three different coordinating anions: chloride, thiocyanide and selenocyanide. The physical properties of these complexes have been investigated in detail.

Introduction

Currently, considerable attention is being paid to supramolecular architectures formed by metal-ion directed self-assembly due to their novel structures, which include helicates,1,2 cages3,4 and interlocked structures.2,5 These supramolecular systems have promising applications in host–guest chemistry,4,6 and often display interesting magnetic properties.7,8 Of particular appeal are metallocycles, grids and squares as they represent comparatively simple systems in which the physico-chemical properties can be tuned. Although some such systems displaying interesting magnetic properties – particularly those exhibiting multiple spin states – have been developed,8,9 their design and synthesis remains a significant challenge.8 For example, in a recent study we reported the self-assembly of a Fe4-molecular square with a hybrid-grid/metallocyclic architecture that contained both high- and low-spin metal centres.8 Herein, we elaborate upon that study to investigate the magnetic and electronic properties of three Co4-molecular squares incorporating the bridging ligand 4,7-phenanthrolino-5,6:5′,6′-pyrazine (ppz) (Scheme 1).

4,7-phenanthrolino-5,6:5′,6′-pyrazine (ppz) is an aromatic system incorporating both pyrazine and pyridyl rings which is both rigid and bisbidentate, and is closely related to the 1,4,5,8,9,12-hexaaza triphenylene (HAT) ligand. Both ppz and HAT have been employed in a number of investigations with transition metals.11,12

Experimental

Materials and procedures

The ligand ppz and all other chemicals and solvents used were of commercial grade and used without further purification. All operations with the Co(II)-containing solutions were performed under a nitrogen atmosphere. UV-vis-NIR spectroscopy was performed on a Cary 5E Spectrophotometer equipped with a Harrick Omni-Diff probe. Spectra are reported as the Kubelka–Munk transform, $F(R)$, as a function of wavelength (cm$^{-1}$). IR spectra were recorded on a Varian 800 Fourier transform infrared spectrometer (as KBr pellets). Magnetic susceptibility data were collected using a Quantum Design Physical Property Measurement System PPMS 5 instrument equipped with a Vibrating Sample Magnetometer (VSM). All measurements were performed on uniform crystalline samples of ~10 mg under an applied field of 0.5 T.

Solid state electrochemical measurements were performed under argon using a Bioanalytical Systems BAS 100A Electrochemical Analyser. Cyclic voltammograms (CVs) were recorded in 0.1 M $[\text{(n-C}_{6}\text{H}_{5})_{4}\text{N}]\text{PF}_6$ dissolved in anhydrous CH$_3$CN at 25 °C using a glassy carbon working electrode (1.5 mm diameter), a platinum wire auxiliary electrode and an Ag/Ag$^+$ wire quasi reference electrode. Solid state samples were mounted on the glassy carbon working electrode by dipping the electrode in the powder sample dispersed in an acetone slurry. Ferrocene was added as an internal

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Scheme 1 Cartoon representation of the self-assembly of a tetranuclear Co(II) molecular square.
standard on completion of each experiment and all potentials are quoted in mV versus Fe'/Fe". To confirm that no dissolution of solid samples was occurring, the material was removed from the electrode surface on completion of each scan and a CV of the bare electrode was performed. In each case, the absence of any redox processes confirmed that no dissolution had occurred.

**Syntheses**

\[\text{[Co(ppz)Cl}_2\text{]-4H}_2\text{O (1). A mixture of ppz (30 mg, 0.129 mmol) and CoCl}_2\text{·6H}_2\text{O (31 mg, 0.129 mmol) in 10 mL water–EtOH (3:2 = v/v) was stirred at 70 °C for 30 min. The solution was subsequently left for overnight to produce X-ray quality orange needle-like crystals. The product was collected by filtration and washed with EtOH, and then allowed to stand in air prior to analysis. Yield: ~91%. UV-vis-NIR (solid state): 9150 cm\(^{-1}\); IR (cm\(^{-1}\), KBr): 3355(br), 3208(m), 1620(w), 1498(m), 1422(m), 1392(s), 1089(m), 802(m), 766(m); elemental analysis (%) calcd. for C\(_{63}\)H\(_{32}\)ClCo\(_4\)N\(_{23}\)O\(_4\)S\(_7\) Fc+/Fc\(_0\). To confirm that no dissolution of solid samples was occurring, the material was removed from the electrode surface on completion of each scan and a CV of the bare electrode was performed. In each case, the absence of any redox processes confirmed that no dissolution had occurred.**

1. \([\text{Co(ppz)}(\text{SCN})(\text{H}_2\text{O})]\cdot\text{ClO}_4\cdot4\text{H}_2\text{O} (2). A solution of a mixture of ppz (25 mg, 0.108 mmol) and Co(ClO\(_4\))\(_2\)·6H\(_2\)O (39.4 mg, 0.108 mmol) in 10 mL water–CH\(_3\)CN (1:1 = v/v) was layered onto an aqueous solution (15 mL) of Co(ClO\(_4\))\(_2\)·6H\(_2\)O (39.4 mg, 0.108 mmol) in 10 mL water–CH\(_3\)CN (1:5 = v/v) was stirred at 70 °C for 30 min. The solution was subsequently left for overnight to produce X-ray quality dark red plate-like crystals. After filtration, the product was washed with CH\(_3\)CN and then allowed to stand in air prior to analysis. Yield: ~77%. UV-vis-NIR (solid state): 9395 cm\(^{-1}\); IR (cm\(^{-1}\), KBr): 3403(br), 3088(m), 2068(s), 1622(m), 1422(m), 1392(s), 810(m), 766(m); elemental analysis (%) calcd. for C\(_{71}\)H\(_{56}\)ClCo\(_4\)N\(_{27}\)O\(_{10}\)Se\(_7\) Fc+/Fc\(_0\). To confirm that no dissolution of solid samples was occurring, the material was removed from the electrode surface on completion of each scan and a CV of the bare electrode was performed. In each case, the absence of any redox processes confirmed that no dissolution had occurred.**

Specific details. The crystals employed in this study rapidly suffered solvent loss and the quality of diffraction data recorded was less than ideal despite rapid handling times and a low temperature collection (few reflections were observed at greater than 1 Å resolution). In addition, there is a large region of smeared electron density present in the lattice. Despite attempts to model this as a number of disordered water molecules with partial occupancies, no satisfactory model could be found. The SQUEEZE function of Platon\(^{19}\) was therefore employed to remove the contribution from this electron density. The molecular weight and density calculations were therefore based upon four water molecules per molecular square.

2. \([\text{Co(ppz)}(\text{SCN})(\text{H}_2\text{O})]\cdot\text{ClO}_4\cdot4\text{H}_2\text{O}·4\text{MeCN} (3). A solution of Co(ClO\(_4\))\(_2\)·6H\(_2\)O (39.4 mg, 0.108 mmol) in 10 mL water–CH\(_3\)CN (1:1 = v/v) was layered onto an aqueous solution (15 mL) of Co(ClO\(_4\))\(_2\)·6H\(_2\)O (39.4 mg, 0.108 mmol) and CoCl\(_2\)·2H\(_2\)O (2.0 mg, 0.041 mmol) in 10 mL water–EtOH (3:2 = v/v). The mixture was stirred at 70 °C for 30 min. The solution was subsequently left for two weeks at room temperature to yield X-ray quality dark red plate-like crystals. After filtration, the product was washed with CH\(_3\)CN and then allowed to stand in air prior to analysis. Yield: ~6%. UV-vis-NIR (solid state): 10310 cm\(^{-1}\); IR (cm\(^{-1}\), KBr): 3403(br), 3088(m), 2068(s), 1622(m), 1587(m), 1487(m), 1392(s), 1092(s), 802(s), 765(m); elemental analysis (%) calcd. for C\(_{65}\)H\(_{32}\)ClCo\(_4\)N\(_{25}\)O\(_{10}\)Se\(_7\) Fc+/Fc\(_0\). To confirm that no dissolution of solid samples was occurring, the material was removed from the electrode surface on completion of each scan and a CV of the bare electrode was performed. In each case, the absence of any redox processes confirmed that no dissolution had occurred.**

Specific details. The perchlorate anion is disordered over three positions and the N(26)-containing thiocyanate was modelled over a number of disordered water molecules with identical thermal parameters. The acetonitrile and water molecules are also disordered and were modelled over a number of positions and the other over three. Disordered atoms in these molecules were included with identical thermal parameters. The acetonitrile and water molecules are also disordered and were modelled over a number of positions and the other over three. Disordered atoms in these molecules were included with identical thermal parameters. The hydroxide atoms of the water molecules could not be located in the difference Fourier map and were not included in the model.

3. \([\text{Co(ppz)}(\text{SeCN})(\text{H}_2\text{O})]\cdot\text{ClO}_4\cdot5\text{H}_2\text{O}·4\text{MeCN} (4). A mixture of ppz (30 mg, 0.108 mmol) and Co(ClO\(_4\))\(_2\)·6H\(_2\)O (43.6 mg, 0.108 mmol) in 10 mL water–CH\(_3\)CN (1:1 = v/v) was stirred at 70 °C for 30 min. The solution was subsequently left for overnight to produce X-ray quality dark red plate-like crystals. After filtration, the product was washed with CH\(_3\)CN and then allowed to stand in air prior to analysis. Yield: ~64%. UV-vis-NIR (solid state): 10310 cm\(^{-1}\); IR (cm\(^{-1}\), KBr): 3403(br), 3088(m), 2068(s), 1622(m), 1587(m), 1487(m), 1392(s), 1092(s), 802(s), 765(m); elemental analysis (%) calcd. for C\(_{65}\)H\(_{32}\)ClCo\(_4\)N\(_{25}\)O\(_{10}\)Se\(_7\) Fc+/Fc\(_0\). To confirm that no dissolution of solid samples was occurring, the material was removed from the electrode surface on completion of each scan and a CV of the bare electrode was performed. In each case, the absence of any redox processes confirmed that no dissolution had occurred.**

Specific details. The perchlorate anion is disordered over two positions and two of the SeCN anions are disordered, one over two positions and the other over three. Disordered atoms in these molecules were included with identical thermal parameters. In an effort to avoid over-parameterisation of the structure, many
of the solvent molecules were refined anisotropically with full occupancy rather than being split over multiple positions. The hydrogen atoms of the water molecules could not be located in the difference Fourier map and were not included in the model.

Results and discussion

Syntheses and X-ray studies

The reaction of cobalt(II) chloride and ppz in a mixture of water and EtOH resulted in a clear orange solution that yielded orange needle-shaped crystals of [Co₄(ppz)₄Cl₈]·4H₂O, 1, in 91% yield. If instead a water/acetonitrile solution of ppz and cobalt perchlorate was layered onto an aqueous solution of potassium thiocyanate, red plate-like crystals of [Co₄(ppz)₄(SCN)₇(OH₂)]ClO₄·4.5H₂O·4MeCN, 2, resulted. Substitution of potassium selenocyanate for potassium thiocyanate yielded red needle-shaped crystals of [Co₄(ppz)₄(SeCN)₇(H₂O)]ClO₄·5H₂O·4MeCN, 3.

The X-ray structure of [Co₄(ppz)₄Cl₈]·4H₂O is given in Fig. 1. The complex crystallises with tetragonal symmetry such that there is one-eighths of the molecule in the asymmetric unit; centring is about the Wyckoff a sites (symmetry 42/m) within P42/nmm. The four high-spin cobalt(II) centres within the molecular square each adopt a cis-orientation and are coordinated to two ppz ligands and two chloride ligands. The bond lengths and angles are typical for octahedral cobalt(II) as is evidenced by the Co–N lengths of 2.141(5) and 2.166(6) Å and the Co–Cl lengths of 2.386(3) Å. The metal centres form a square planar array with a 7.1 Å separation between adjacent sites. Each of the ppz ligands alternates pointing up and down in an almost grid-like fashion, resulting in a substantial void space within the cavity of the molecular square. Platon estimates that 37% of the unit cell represents a solvent accessible void.

Fig. 2 Space filling representation showing part of the crystal packing of [Co₄(ppz)₄Cl₈]·4H₂O viewed down the c-axis.

Fig. 3 Schematic representation of the crystal structure of [ClO₄₋₃Co₄(ppz)₄(SCN)₇(OH₂)]·4.5H₂O·4MeCN. Solvent molecules are removed for clarity. The perchlorate anion is shown in a space filling representation.

The crystal structure of 2 (Fig. 3) reveals a Co₄(ppz)₄ unit that is very similar to that of 1. The complex crystallises in the monoclinic P2₁/n space group with one molecule per asymmetric unit, which is of lower symmetry than that found in 1. The high-spin octahedral cobalt(II) centres are again arranged in a close to planar array, although the Co–Co distances now range from 7.1–7.2 Å. In contrast to 1, the coordination geometry of each ‘corner’ is not identical. While three ‘corners’ are each bound to two ppz ligands and two SCN⁻ ligands, one anion on the fourth centre has been replaced with a solvent water molecule such that the supramolecular square is best described as [Co₄(ppz)₄(SCN)₇(OH₂)]⁺. Once again, the bond lengths are typical for octahedral cobalt(II) with the Co–N aromatic lengths bonding (2.65 Å) forming an infinite 3D-network, suggesting that this complex could be a promising target for host–guest or gas-sorption investigations.

The crystal structure of 3 (Fig. 4) reveals a Co₄(ppz)₄ unit that is very similar to that of 1. The complex crystallises in the monoclinic P2₁/n space group with one molecule per asymmetric unit, which is of lower symmetry than that found in 1. The high-spin octahedral cobalt(II) centres are again arranged in a close to planar array, although the Co–Co distances now range from 7.1–7.2 Å. In contrast to 1, the coordination geometry of each ‘corner’ is not identical. While three ‘corners’ are each bound to two ppz ligands and two SCN⁻ ligands, one anion on the fourth centre has been replaced with a solvent water molecule such that the supramolecular square is best described as [Co₄(ppz)₄(SCN)₇(OH₂)]⁺. Once again, the bond lengths are typical for octahedral cobalt(II) with the Co–N aromatic lengths bonding (2.65 Å) forming an infinite 3D-network, suggesting that this complex could be a promising target for host–guest or gas-sorption investigations.
ranging from 2.14 Å to 2.21 Å and Co–N thiocyanate bond lengths from 2.04 Å to 2.14 Å. The Co–O bond length is also typical at 2.049(3) Å.

The charge of the molecular square is accounted for by the presence of a perchlorate anion, which is located within the cavity of the [Co₄(ppz)₄(SCN)₇(OH₂)]⁺ unit (therefore best described as [ClO₄⁺Co₄(ppz)₄(SCN)₇(OH₂)] and displaced from the Co₄ plane by 3.12 Å (measured to the Cl atom). Also lying partially within the cavity is an acetonitrile molecule, which sits directly above/below the perchlorate anion. The crystal packing is very similar to that in 1, with strong π–π and weak CHphenylene–anion interactions resulting in the formation of a 3D network housing 1D channels that extend along the crystallographic b-axis. These channels are filled with the anion and the residual water and acetonitrile solvent molecules.

The crystal structure of 3 (Fig. 4) is isomorphous with that of 2, with the replacement of SCN⁻ ligands by SeCN⁻ resulting in a formula of [Co₄(ppz)₄(SeCN)₇(OH₂)] · ClO₄ · 5H₂O · 4MeCN. Once again, a perchlorate anion occupies the central cavity of the molecular square. The crystal packing is dominated by π–π stacking and weak hydrogen bonding resulting in the formation of channels that are filled with anions, water and acetonitrile solvent molecules. The bond lengths and Co–Co separations are very similar to those given for 2 above.

Vibrational and electronic spectroscopy

The solid state IR spectra of complexes 2 and 3 at 298 K exhibit intense ν(CN) bands at 2080 and 2068 cm⁻¹. The solid state UV-vis-NIR spectra of the molecular squares over the region 5000–28 000 cm⁻¹ (Fig. 5) revealed a low intensity forbidden d–d transition which was attributed to the high spin d⁷ Co²⁺ centres at 9150, 9395 and 10 310 cm⁻¹ for 1, 2 and 3, respectively. The increase in the energy of this feature upon variation of the coordinated anion from Cl⁻ (1) to SCN⁻ (2) and SeCN⁻ (3) is consistent with the transition from a weak field ligand such as Cl⁻ to increasingly stronger field ligands. A series of broad, high intensity metal-to-ligand (MLCT) charge transfer bands were also observed in the visible region of the spectra, with the energy of the band edge increasing in the order 3 < 2 < 1. The latter reflects the increasing stabilisation of the complexes as the ligand field of the coordinated anion decreases from SeCN⁻ in 3, to SCN⁻ in 2 and Cl⁻ in 1.

Magnetism

The magnetic susceptibilities, χ, for compounds 1–3 were measured over the range 3–290 K (Fig. 6). The three compounds exhibit similar magnetic behaviour with room temperature χT values of 11.2, 10.5 and 8.77 cm³ K mol⁻¹, respectively, for 1, 2 and 3. This is consistent with four Co(II) ions with S = 3/2 (high-spin) in an octahedral environment with g values of 2.44, 2.37 and 2.16 for 1, 2 and 3, respectively.
Below 125 K, the magnetic susceptibility of compounds 1–3 starts to decrease, reaching 7.22 cm³ K mol⁻¹ for 1, 6.30 cm³ K mol⁻¹ for 2 and 3.83 cm³ K mol⁻¹ for 3 at 3 K. In octahedral Co(II) compounds the effects of spin orbit coupling and crystalline distortions combine to give a spin-doublet ground state.²⁹ Spin orbit coupling contributes to both the anisotropy of the g factor and to zero field splitting effects.²² Significantly, anisotropic spin moments have been reported in the literature for Co compounds in octahedral environments.²¹ A larger anisotropy of the g value is expected as the crystal field becomes more distorted. As was evident from the UV-Vis-NIR spectra, the ligand field in compounds 1–3 increases in the order Cl⁻ < SCN⁻ < SeCN⁻, which is consistent with the increase in g values for 1–3. Below 125 K, the magnetic behaviour of the three compounds is mainly due to zero field splitting effects; however, the possibility of magnetic interactions cannot be excluded. Given that the Co···Co separation distance along the ppz bridging ligand is equal to or larger than 7.1 Å in the three compounds, the magnetic interactions, if any, should be small and cannot be distinguished from the overall zero field splitting effect. Indeed, in Co(HAT)(N(CN)₃)(OH₂), where similar Co···Co distances along the HAT ligand were reported, the magnetic interactions were found to be negligible.²²

Electrochemistry

Solid state cyclic voltammetry of the complexes in 0.1 M ([n-C₄H₉]₄N)PF₆/CH₂CN electrolyte revealed a series of broad overlapping redox processes in the region 500–2000 mV (versus the ferrocene/ferroenium couple) on the forward potential sweep from 0–2000 mV. Fig. 7 shows a representative CV for 2 which displays the characteristic irreversible redox process corresponding to Co²⁺/³⁺ oxidation. Interestingly, at least two peaks at ~1145 and 1250 mV can be discerned for oxidation in the first cycle; however, no resolution of these processes could be achieved. Square wave and differential pulse methods were also investigated in an attempt to separate the individual redox couples. The almost simultaneous oxidation of the four Co²⁺ centres suggests that only weak electronic coupling exists between the metal centres via the bridging ppz ligands. Complexes 1 and 3 exhibit similar irreversible Co²⁺/³⁺ redox processes at 926 and 1475 mV. Notably, the anodic shift in the metal centred potential (i.e., 1 < 2 < 3) mirrors the trend in the ligand field observed from UV-Vis-NIR and magnetic data, i.e., Cl⁻ is a weak field ligand compared with SCN⁻ and SeCN⁻.

Conclusion

We have prepared three new tetracnuclear cobalt(II) molecular squares based on the bridging ligand 4,7-phenanthroline-5,6:5′,6′-pyrazine (ppz) with different coordinated counter ions. These structures have been characterised by X-ray crystallography. Magnetic measurements indicate similar behaviour for the three compounds with each consisting of four high spin Co(II) ions in an octahedral environment. A larger anisotropy of the g value is found as the ligand field effect increases for compounds 1–3 with the change in the coordinated anion from Cl⁻ to SCN⁻ to SeCN⁻. The electrochemical data as well as the energies of the forbidden d–d transitions for Co(II) in the UV-Vis-NIR spectra of the complexes confirmed the trend towards increasingly stronger field ligands (Cl⁻ < SCN⁻ < SeCN⁻). At low temperatures, the magnetic behaviour is dominated by zero field splitting effects. Further investigations of the chemical and physical properties of the ppz ligand with other metal ions are ongoing, with particular interest in the interplay between the magnetic, optical and electronic properties of the supramolecular systems.

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References


