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Cobalt(II) and iron(II) bis(2,2′ : 6′,2″-terpyridine) complexes functionalized with alkynes and cobalt carbonyl clusters†

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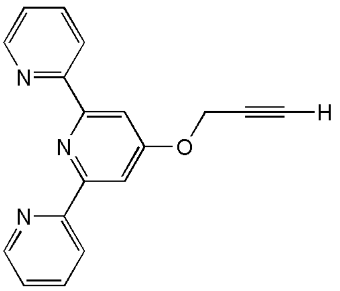
The preparation and characterization of new cobalt(II) and iron(II) complexes containing alkyne or cobalt cluster functionalized 2,2′ : 6′,2″-terpyridine ligands are described. The cobalt(II) complexes exhibit paramagnetically shifted, but well-resolved, ^{1}H NMR spectra that are characteristic of low-spin cobalt(II) solution species. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: 2,2′ : 6′,2″-terpyridine; cobalt(II); iron(II); carbonyl cluster; alkyne

INTRODUCTION

The use of 2,2′ : 6′,2″-terpyridine (tpy) as a metal-binding domain has been central to our interests in the design of metallosupramolecular assemblies (e.g. see Ref. 1). An advantage of the octahedral $\{M(tpy)_2\}^{n+}$ domain over the more commonly encountered octahedral $\{M(bpy)_3\}^{n+}$ (bpy = 2,2′-bipyridine) motif is that the latter is inherently chiral, whereas the former is not. Moreover, introducing substituents X into the two 4′-positions (Scheme 1) generates a linear X–M–X array with the X groups, therefore, remote from one another. Recently, we have made significant progress in assembling molecules that contain both Werner-type coordination and organometallic, including cluster, domains.[2–10] Among these systems is the diamagnetic complex $[Ru(\mathbf{1})_2]^{2+}$, which reacts with $Co_2(CO)_8$ to generate $[Ru(\mathbf{2})_2]^{2+}$ containing cluster-functionalized ligands.[2,4] Metal carbonyl clusters in paramagnetic systems are rare,[11] and in most cases the examples of cluster radical anions arise from electrochemical reduction.[12–16] An interesting example of a paramagnetic metal carbonyl species is $Fe_2(CO)_8\{Mn(thf)_2\}_2$ (thf = tetrahydrofuran), which has been described as being intermediate between a system that contains zero-valent metals and one composed of $[Fe(CO)_4]^{2-}$ and $[Mn(thf)_2]^{2+}$ ions.[17] Our approach in the work reported here is to introduce a paramagnetic Co^{2+} centre within a bis(tpy) domain, and assemble metal carbonyl cluster domains at the peripheries of the complex.



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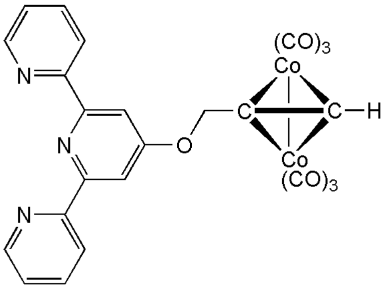

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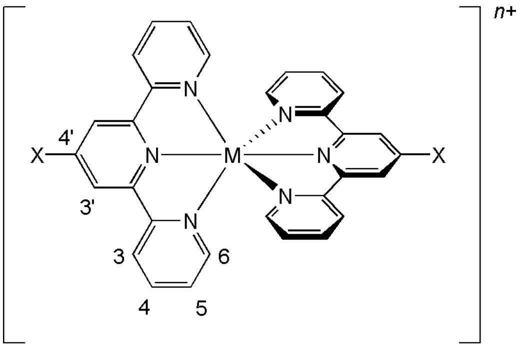
†Dedicated to Professor Thomas P. Fehlner on the occasion of his 65th birthday, in recognition of his outstanding contributions to organometallic and inorganic chemistry.



Scheme 1.

EXPERIMENTAL

General

All reactions were carried out under nitrogen and solvents were distilled before use and were oxygen free; water was oxygen free. FT-NMR spectra were recorded on a Bruker AC 300 spectrometer at ambient temperature. ^1H and ^{13}C NMR shifts are reported with respect to δ 0 for Me_4Si. IR spectra were recorded on a Shimadzu FTIR-8300 series spectrophotometer fitted with a Golden Gate ATR; all samples were neat solids. UV–vis spectra were measured on a Shimadzu UV-3101PC spectrophotometer. Electrospray mass spectrometry (ES-MS) was undertaken using a Micromass LCT-mass spectrometer in MeOH. Ligand **1** was prepared as previously reported.[5] Atom numbering for the tpy ligand is given in Scheme 1.

$[Fe(1)_2][PF_6]_2$

$FeCl_2{\cdot}4H_2O$ (14 mg, 0.070 mmol) and ligand **1** (40 mg, 0.14 mmol) were dissolved in a MeCN/MeOH mixture (10 ml/10 ml) and stirred at room temperature for 1 h to give a purple solution. Aqueous $[NH_4][PF_6]$ was added and the resulting precipitate collected on cotton wool. The precipitate was washed with water to yield a purple solid (36 mg, 56%).

^1H NMR (CD_3CN, 300 MHz): δ 8.50 (s, 4H, $H^{3'}$), 8.43 (d, J 8.1 Hz, 4H, H^3), 7.87 (td, J 7.4, 1.8 Hz, 4H, H^4), 7.14 (d, J 4.2 Hz, 4H, H^6), 7.08 (td, J 6, 1.2 Hz, 4H, H^5), 5.35 (d, J 2.1 Hz, 4H, CH_2), 3.17 (t, J 2.3 Hz, 2H, alkyne CH). ^{13}C NMR (CD_3CN, 75 Hz) δ 167.8, 162.2, 159.0, 154.6, 139.8, 128.6, 124.8, 112.6, 79.5, 78.0, 59.1. UV–vis (CH_3CN): λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 243 (69.7), 272 (66.4), 315 (57.4), 362 (9.6), 504 (13.2), 554 (18.6). IR ($\overline{\upsilon}$, cm^{-1}): 3287 w, 2959 w, 2928 w, 2862 w, 1728 m, 1612 m, 1555 m, 1470 m, 1423 m, 1211 s, 826 s $[PF_6]$, 787 s, 752 m. ES-MS m/z 775 $[M - PF_6]^+$ with satisfactory isotopic matching to simulated spectrum.

$[Fe(2)_2][PF_6]_2$

$[Fe(1)_2][PF_6]_2$ (20 mg, 0.022 mmol) was dissolved in dry MeCN (1 ml), and solid $Co_2(CO)_8$ (54 mg, 0.16 mmol) was added to the solution. After stirring the reaction mixture for 1 h, the solvent was removed. The impure purple solid showed bands in the IR spectrum at 2098, 2056 and 2021 cm^{-1} ($\overline{\upsilon}$ (CO)), and spot thin-layer chromatography (TLC) indicated the presence of at least two products. An attempt was made to purify the product by column chromatography (see text).

$[Co(1)_2][PF_6]_2$

$[Co(O_2CMe)_2]{\cdot}4H_2O$ (17 mg, 0.068 mmol) and ligand **1** (40 mg, 0.14 mmol) were dissolved in a mixture of MeCN (10 ml) and MeOH (10 ml) and stirred at room temperature for 1 h. Aqueous $[NH_4][PF_6]$ was added and the resulting precipitate was collected on cotton wool. The precipitate was washed with water to give an orange solid (31 mg, 48%). ^1H NMR (CD_3CN, 300 MHz): δ 114 (broad, 4H), 74.9 (s, 4H), 71.1 (s, 4H), 35.3 (s, 4H), 14.6 (s, 4H, CH_2), 6.40 (s, 4H), 6.27 (s, 2H, alkyne CH); see text for tpy H assignments. UV–vis (CH_3CN): λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$) 244 (100.2), 269 (77.1), 307 (53.2). IR ($\overline{\upsilon}$, cm^{-1}): 3283 w, 1717 w, 1616 m, 1558 m, 1508 w, 1474 m, 1439 m, 1219 m, 829 s $[PF_6]$, 791 s, 745 m. ES-MS m/z 778 $[M - PF_6]^+$ with satisfactory isotopic matching to simulated spectrum.

$[Co(2)_2][PF_6]_2$

$[Co(1)_2][PF_6]_2$ (20 mg, 0.022 mmol) was dissolved in dry MeCN (1.0 ml). To this solution was added $Co_2(CO)_8$ (54 mg, 0.16 mmol) and the reaction mixture was stirred for 1 h. The solvent was removed at room temperature under vacuum, and the residue was washed with hexane to remove unreacted $Co_2(CO)_8$. Spot TLC showed one product and no further purification was carried out. The product was orange (26 mg, 80%). ^1H NMR (CD_3CN, 300 MHz): δ 113 (broad, 4H), 74.8 (s, 4H), 70.8 (s, 4H), 35.0 (s, 4H), 15.6 (s, 4H, CH_2), 10.21 (s, 2H, alkyne CH), 6.48 (s, 4H); see text for tpy H assignments. IR ($\overline{\upsilon}$, cm^{-1}): 2098 m, 2056 s, 2025 s [CO], 833 s $[PF_6]$. ES-MS m/z 1350 $[M - PF_6]^+$ with satisfactory isotopic matching to simulated spectrum.

RESULTS AND DISCUSSION

We have previously described the preparation and characterization of the diamagnetic ruthenium(II) complex $[Ru(1)_2][PF_6]_2$ and its reaction with $Co_2(CO)_8$ to give $[Ru(2)][PF_6]_2$.[2] We now report the preparations of the diamagnetic complex $[Fe(1)_2]^{2+}$ and paramagnetic $[Co(1)_2]^{2+}$, and their reactions with $Co_2(CO)_8$.

Ligand **1** reacts with $FeCl_2{\cdot}4H_2O$ to afford, after treatment with $[NH_4][PF_6]$, $[Fe(1)_2][PF_6]_2$. The highest mass peak in the electrospray mass spectrum of the product is at $m/z = 775$ and is assigned as $[M - PF_6]^+$. The ^1H NMR spectrum of $[Fe(1)_2]^{2+}$ exhibits signals for the tpy domain, the pattern of which differs from those in the ruthenium(II) analogue.[2] They can be assigned on the basis of the coupling patterns and coupling constants, and by comparison with the signals from related complexes. In the pendant functional group, the methylene group gives rise to a doublet (J 2.1 Hz) at δ 5.35, and a triplet (*J* 2.3 Hz) at δ 3.17 is assigned to the terminal alkyne CH group. These signals compare with δ 5.27 (*J* 2.4 Hz) and δ 3.14 (*J* 2.4 Hz) in $[Ru(\mathbf{1})_2][PF_6]_2$.[2] The ^{13}C NMR spectrum of a CD_3CN solution of $[Fe(\mathbf{1})_2][PF_6]_2$ shows the expected 11 signals at chemical shifts that are close to those of the ruthenium(II) analogue.

The cobalt(II) complex $[Co(\mathbf{1})_2][PF_6]_2$ results from the reaction of cobalt(II) acetate and ligand **1**, and a peak in the electrospray mass spectrum at $m/z = 778$ corresponds to $[M - PF_6]^+$. A cobalt(II) ion possesses a d^7 configuration and, in a near octahedral environment, is paramagnetic irrespective of whether the complex is low-spin ($t_{2g}^6 e_g^1$) or high-spin ($t_{2g}^5 e_g^2$). (Although $[Co(\mathbf{1})_2]^{2+}$ does not possess O_h symmetry, these electronic configurations can be used to a first approximation.) The ^1H NMR spectrum of a CD_3CN solution of $[Co(\mathbf{1})_2]^{2+}$ is shown in Fig. 1. All signals are paramagnetically shifted and can be compared with those previously reported for $[Co(tpy)_2]^{2+}$ and $[Co(6\text{-}Brtpy)_2]^{2+}$ (6-Brtpy = 6-bromo-2,2′ : 6′,2″-terpyridine).[18] Leaving aside the asymmetry introduced by the 6-bromo substituent, the ^1H NMR spectra of $[Co(6\text{-}Brtpy)_2]^{2+}$ and $[Co(tpy)_2]^{2+}$ are significantly different because of the chemical shift range over which the signals are dispersed. The six signals in low-spin $[Co(tpy)_2]^{2+}$ fall in the range δ 9 to 99, whereas the resonances for high-spin $[Co(6\text{-}Brtpy)_2]^{2+}$ range up to δ 250. By comparison with these compounds, we assign $[Co(\mathbf{1})_2]^{2+}$ as a low-spin Co^{2+} complex. All protons in $[Co(\mathbf{1})_2]^{2+}$ experience the effects of the paramagnetic Co^{2+} centre, as is clear from a comparison of the chemical shifts for $[Co(\mathbf{1})_2]^{2+}$ with those of diamagnetic $[Fe(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{1})_2]^{2+}$. Proton H^6 of the tpy domain is spatially the closest to the metal(II) centre and is assigned to the signal at δ 114. In $[Fe(\mathbf{1})_2]^{2+}$ and $[Ru(\mathbf{1})_2]^{2+}$, this signal comes at δ 7.14 and 7.38[2] respectively. The signal for H^6 in $[Co(\mathbf{1})_2]^{2+}$ becomes very broad (line-width at half peak height is 160 Hz), due to the extremely efficient relaxation mechanism arising from coupling between the proton nuclear spin and the electron spin of the Co^{2+} centre. The signals for the CH_2 and CH(alkyne) protons shift from δ 5.35 (CH_2) and 3.17 (alkyne CH) in $[Fe(\mathbf{1})_2]^{2+}$ to 14.6 (CH_2) and 6.27 (alkyne CH) in $[Co(\mathbf{1})_2]^{2+}$ (Fig. 1); the line widths of the signals in the cobalt(II) complex preclude the observation of coupling as was observed in the iron(II) complex. Compared with the signals arising from the tpy ring protons, those assigned to the 4′-substituent protons are sharp. The line-widths at half-height for the signals at δ 74.9, 71.1, 35.3 and 6.40 are 20.2, 22.8, 15.5 and 13.0 Hz respectively compared with values of 5.4 and 3.6 Hz respectively for the signals at δ 14.6 (CH_2) and 6.27 (CH alkyne). Assignments of signals in the ^1H NMR spectrum of $[Co(\mathbf{1})_2]^{2+}$ to the tpy protons is not trivial, since conventional correlation spectroscopy techniques suffer from the very short T_1 values, which permit minimal time for spin transfer. Preliminary NMR spectroscopic studies

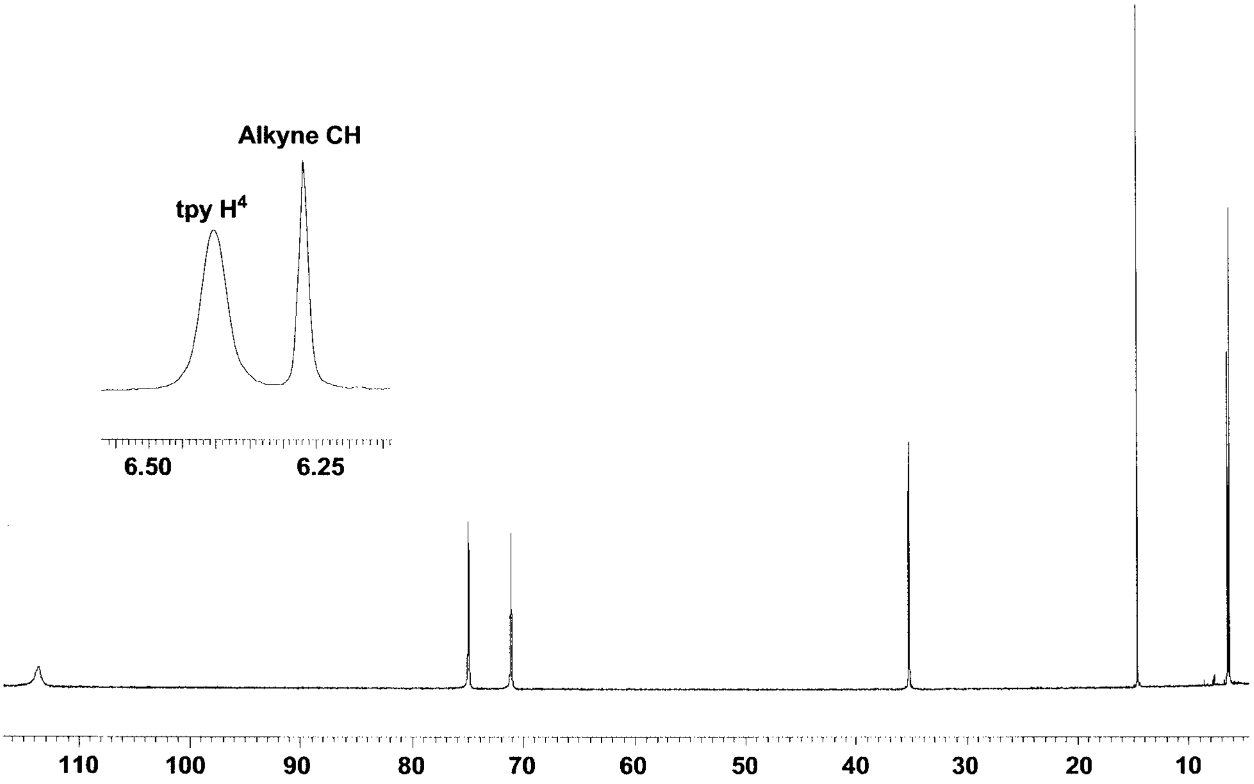


Figure 1. 300 MHz ^1H NMR (CD_3CN, 298 K) spectrum of $[Co(\mathbf{1})_2][PF_6]_2$. The inset is an expansion of the peaks assigned to the CH_2 and alkyne CH protons of the pendant functional group.

on a range of homoleptic cobalt(II) complexes containing ligands of the type 4′-RCH_2Otpy and 4′-RNHtpy[19] allow us to make preliminary assignments in $[Co(\mathbf{1})_2]^{2+}$ (see Scheme 1) as follows: δ 113.5 (H^6), 74.9 ($H^{3'}$), 71.1 (H^3), 35.3 (H^5) and 6.40 (H^4). Despite the paramagnetic nature of $[Co(\mathbf{1})_2]^{2+}$, Fig. 1 clearly illustrates that ^1H NMR spectroscopy remains a useful tool for characterization of Co(II) bis(tpy) complexes, since the resonances remain relatively well-resolved.

The reaction of $[Fe(\mathbf{1})_2]^{2+}$ with an excess of $Co_2(CO)_8$ was carried out at room temperature in MeCN, and was monitored by IR spectroscopy. The appearance of absorptions at 2098, 2056 and 2021 cm^{-1} indicated that the alkyne units had reacted with $Co_2(CO)_8$ in the desired manner and that $[Fe(\mathbf{2})_2]^{2+}$ and/or $[Fe(\mathbf{1})(\mathbf{2})]^{2+}$ had been formed. In $[Ru(\mathbf{2})_2]^{2+}$, the $C_2Co_2(CO)_6$ cluster units give rise to characteristic bands at 2099, 2059 and 2029 cm^{-1}, and related complexes show similar patterns of strong absorptions.[2] Attempts to purify the $[Fe(\mathbf{2})_2]^{2+}$ product by chromatography on SiO_2 were unsuccessful, and mass spectrometric and ^1H NMR spectroscopic data were consistent with the isolation of $[Fe(4'\text{-HOtpy})_2]$ instead of $[Fe(\mathbf{2})_2][PF_6]_2$. Cleavage of the ether bridge to generate the coordinated 4′-HOtpy ligand in this type of complex is not without precedent.[2] Since a single iron(II) product could not be obtained without separation, this reaction was not pursued further.

The reaction of $[Co(\mathbf{1})_2]^{2+}$ with an excess of $Co_2(CO)_8$ in MeCN led to the formation of an orange solid after removal of solvent. After washing with hexane, TLC and spectroscopic data indicated that a single product had been formed. The electrospray mass spectrum showed a peak at m/z 1350 corresponding to $[Co(\mathbf{1})_2PF_6]^+$, and in the IR spectrum of the complex the characteristic pattern of absorptions at 2098, 2056 and 2025 cm^{-1} indicated the presence of the $C_2Co_2(CO)_6$ cluster unit. The conversion of the diamagnetic $[Ru(\mathbf{1})_2]^{2+}$ to $[Ru(\mathbf{2})_2]^{2+}$ is accompanied by a shift of the ^1H NMR signal for the terminal CH proton from δ 3.14 to 6.57, whereas the signal due to the methylene protons is much less responsive to the structural and electronic change (δ 5.27 to 5.82).[2] In paramagnetic $[Co(\mathbf{1})_2]^{2+}$, the CH_2 and the terminal alkyne protons give rise to signals that are already shifted to higher frequency (δ 14.6 and 6.27 respectively; Fig. 1). After reaction with $Co_2(CO)_8$, these signals have completely disappeared and are replaced by resonances at δ 15.6 (CH_2) and 10.21 (alkyne CH). Figure 2 shows the region of the ^1H NMR spectrum of $[Co(\mathbf{2})_2][PF_6]_2$ with signals comparable to those in the inset in Fig. 1. The signals assigned to the tpy protons in $[Co(\mathbf{2})_2][PF_6]_2$ (δ 113 (H^6), 74.8 ($H^{3'}$), 70.8 (H^3), 35.0 (H^5), 6.48 (H^4)) are little shifted from those in $[Co(\mathbf{1})_2][PF_6]_2$, and they exhibit the same degree of broadening discussed earlier. The ^1H NMR spectroscopic data are in accord with the formulation of the symmetrical product $[Co(\mathbf{2})_2]^{2+}$ rather than a heteroleptic species $[Co(\mathbf{1})(\mathbf{2})]^{2+}$, and confirm that complete reaction of the alkyne functional groups in $[Co(\mathbf{1})_2]^{2+}$ has occurred. We have been unable to obtain single crystals of $[Co(\mathbf{2})_2][PF_6]_2$; however, based on structural data for $[Ru(\mathbf{1})_2][PF_6]_2\cdot Me_2CO$,[2] the modelled structure (not optimized) of $[Co(\mathbf{2})_2]^{2+}$ (also representative of the structure of $[Fe(\mathbf{2})_2]^{2+}$) has been generated and is shown in Fig. 3. This illustrates the spatial disposition of the two cluster units with respect to the $\{Co(tpy)_2\}$ domain.

CONCLUSIONS

We have extended previous methodology to prepare alkyne-functionalized bis(tpy) complexes of iron(II) and cobalt(II); this has allowed us to compare the ^1H NMR spectroscopic properties of two isostructural complexes, which are diamagnetic and paramagnetic respectively. The pendant alkyne groups in $[Co(\mathbf{1})_2]^{2+}$ are readily converted into cobalt-carbonyl-containing cluster units, giving diamagnetic or paramagnetic cluster-functionalized iron(II) or cobalt(II) bis(tpy) complexes respectively.

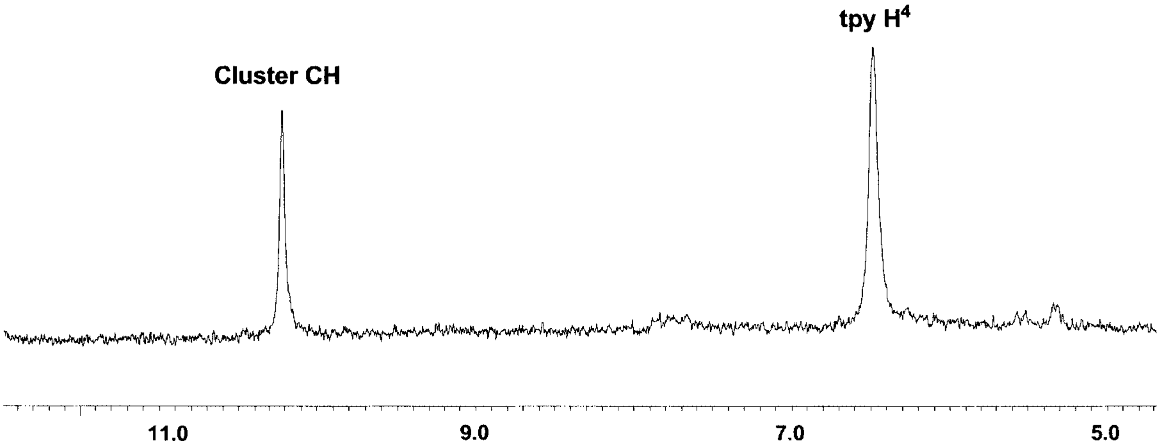


Figure 2. Part of the 300 MHz ^1H NMR (CD_3CN, 298 K) spectrum of $[Co(\mathbf{2})_2][PF_6]_2$, for comparison with the inset in Fig. 1.

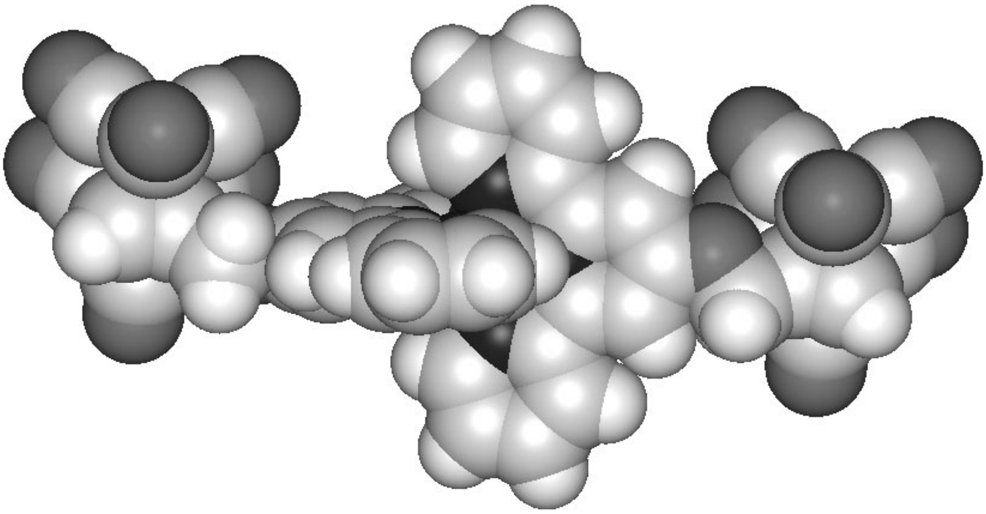


Figure 3. Space-filling diagram of the modelled structure of $[Co(\mathbf{2})_2]^{2+}$ (non-optimized). The nitrogen and oxygen atoms are shown in black, and the cobalt atoms are hidden.

Acknowledgements

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