Old ligands with new coordination chemistry: Linear trinuclear mixed oxidation state cobalt(III/II/III) complexes and their mononuclear "ligand" cobalt(III) complexes featuring 2-pyridyloximates

Theocharis C. Stamatatos [a], Aidan Bell [b], Paul Cooper [b],
Aris Terzis [c], Catherine P. Raptopoulou [c], Sarah L. Heath [b],
Richard E.P. Winpenny [b,*], Spyros P. Perlepes [a,*]

[a] Department of Chemistry, University of Patras, 265 04 Patras, Greece
[b] School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, UK
[c] Institute of Materials Science, NCSR "Demokritos", 153 10 Aghia Paraskevi Attikis, Greece

Abstract

Reaction schemes involving 2-pyridyloximes, (py)C(R)NOH, Co^{II} sources and counterions X^- in various solvents lead to the new family of linear trinuclear clusters $[Co_3^{III,II,III}\{(py)C(R)NO\}_6]X_2$ (py = 2-pyridyl group; R = H, Me, Ph; X = ClO_4, PF_6). The outer metal centres are low spin, octahedral Co^{III} ions and are coordinated by three N,N'-bound 2-pyridyloximato ligands; each of these outer Co^{III} complexes acts as a tridentate chelating "ligand" to the central Co^{II} ion, which adopts an octahedral geometry with six oxygen donor atoms. The Co^{III} "ligands" have been individually prepared and the reaction of $[Co^{III}\{(py)C(Me)NO\}_3]$ with $Co(ClO_4)_2 \cdot 6H_2O$ leads to the isolation of $[Co_3^{III,II,III}\{(py)C(Me)NO\}_6](ClO_4)_2$.
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The enormous increase in the attention paid to magnetic 3d-metal clusters has been mainly due to the discovery that molecular species can show slow relaxation of magnetisation under certain circumstances [1]. These molecular species, named "single-molecule magnets" (SMMs), have attracted great interest from both a technological viewpoint – in that such single molecules are the smallest conceivable memory devices – and from a fundamental scientific perspective, as the clusters have allowed studies of quantum mechanical phenomena such as tunnelling [1].

Ligands used in synthesising 3d-metal clusters are however comparatively restricted and, thus, discovery of new families of ligands remains important in this field. With this aim, we are exploring "ligand blend" reactions involving carboxylates and the monoanions of 2-pyridyloximes (Scheme 1) as a means to high-nuclearity 3d-metal species. Our first results have been very encouraging, and a series of Mn complexes with nuclearities ranging from 1 to 10 and with interesting properties (including high-spin molecules) have been prepared [2].
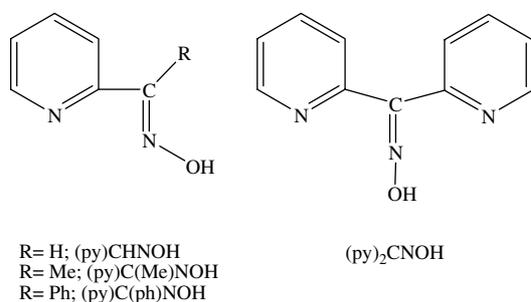
Scheme 1. Formulae and abbreviations of the 2-pyridyloxime ligands discussed in the text.

Remarkable features of the performed reactions were in situ, metal-ion assisted transformations of amounts of 2-pyridinealdoxime [(py)CHNOH] [2c] and di-2-pyridyl ketone oxime [(py)$_2$CNOH] [2a,2e] to yield coordinated ligands that were not used as reactants. 2-pyridyl oximes are "old" ligands [3]. However, there is currently [4,5] a renewed interest in their coordination chemistry; these efforts are driven by a number of considerations, including the solution of pure chemical problems, the synthesis of metallacrowns, and the employment of 2-pyridyloximate ligands in the isolation of homometallic and heterometallic clusters and polymers with exciting magnetic properties.

Cobalt(II) and cobalt(III) remain today as enticing and rewarding centres in coordination chemistry [6a], with cobalt(II) clusters being promising players in the field of SMMs [6b,6c]. It is thus surprising that cobalt complexes featuring oximate ligands are rare [4]. We have just reported [7] that employment of (py)$_2$CNOH (Scheme 1) in cobalt carboxylate chemistry allows the isolation of the first Co members in the family of metallacrowns. Here, we report studies of the reactions of (py)CHNOH, methyl 2-pyridyl ketone oxime [(py)C(Me)NOH] and phenyl 2-pyridyl ketone oxime [(py)C(ph)NOH] with cobalt(II) sources, which result in the preparation of linear trinuclear mixed-valence Co$_2^{III}$Co^{II} clusters and their mononuclear Co^{III} constituents. The present study can be regarded as the amalgamation of our interests in the areas of polynuclear Co chemistry [7,8] and coordination chemistry of 2-pyridyloximes [2,7].

Reaction of Co(O$_2$CMe)$_2 \cdot$ 4H$_2$O with two equivalents of (py)C(ph)NOH and one equivalent of NH$_4$PF$_6$ in MeCN, in the presence of atmospheric oxygen, under reflux for 2 h and layering of Et$_2$O onto the resulting red solution gave dark red crystals of complex [Co$_3${(py)-C(ph)NO}$_6$](PF$_6$)$_2 \cdot$ 6MeCN (**1** · 6MeCN)[1] in 70% yield. Complex **1** can also be isolated in good yields (>50%) from the CoCl$_2 \cdot$ 6H$_2$O/(py)C(ph)NOH/Me$_4$NOH/NH$_4$PF$_6$ (1:2:2:1) reaction mixture in MeCN or MeOH.

The crystal structure[2] of **1** · 6MeCN reveals the formation of a linear trinuclear cation (Fig. 1). The central metal ion, Co(2), which is located on a crystallographic inversion centre, is octahedrally coordinated by six oxygen atoms belonging to six (py)C(ph)NO$^-$ ligands. The six sites on each of the distorted octahedral, terminal Co ions are occupied by the nitrogen atoms that belong to the "chelating" part of three (py)C(ph)NO$^-$ ligands, with the three oximate N atoms in the facial (or *cis*) configuration. Charge considerations require a formal 2Co^{III}, Co^{II} description of **1**, and the terminal metal ions are clearly low-spin Co^{III} ions based on their Co–N bond lengths (all <1.96 Å), which have lengths similar to Co^{III}–N bond lengths in other structurally characterised cobalt(III) complexes with N-ligation [6a,9]. The central cobalt centre [Co(2)] has Co–O distances in the range 2.077(3)–2.127(3) Å, indicating that this is a Co^{II} ion [9]. The above assignments of the Co oxidation states are confirmed by BVS calculations [10], which give values of 2.87 and 2.01 for Co(1) and Co(2), respectively. The (py)C(ph)NO$^-$ ions function as η^1:η^1:η^1:μ_2 ligands (or as 2.1$_1$1$_2$1$_2$ ligands using Harris notation [11]); each ligand (Scheme 2) chelates one Co^{III} ion through the 2-pyridyl and the oximate nitrogen atoms forming a five-membered chelating ring, and bridges this metal centre with the central Co^{II} ion through the terminally ligated, deprotonated oxygen atom. Complex **1** joins a handful of structurally characterised linear, valence-trapped Co^{III}Co^{II}Co^{III} clusters [12].

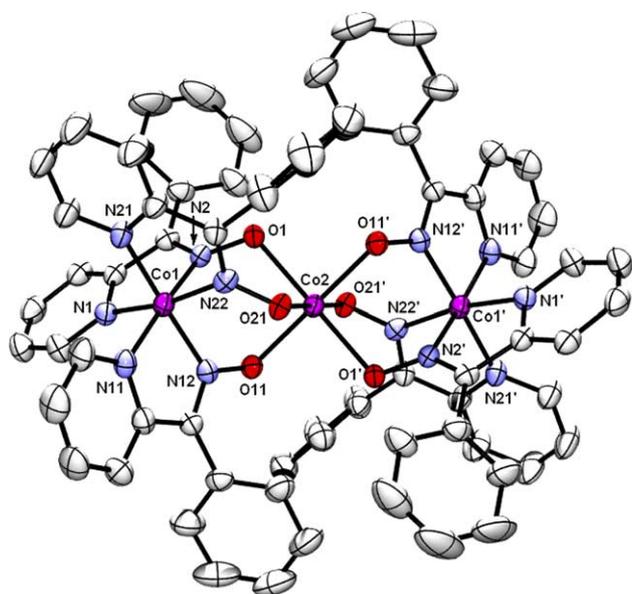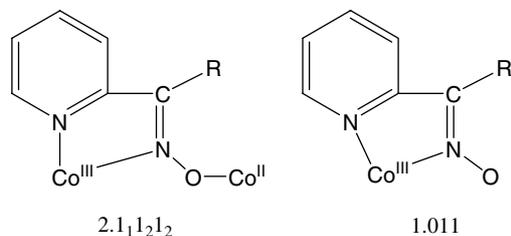The fact that the two mononuclear neutral *fac*-[Co^{III}{(py)C(ph)NO}$_3$] units of **1** can be considered as acting as tridentate chelating "ligands" to the central

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Fig. 1. Molecular structure of the mixed-valence (III/II/III) cation $[Co_3\{(py)C(ph)NO\}_6]^{2+}$ present in complex $1 \cdot 6MeCN$ with selected atom labelling. Primes are used for symmetry-related $(-x, -y, -z)$ atoms. Selected interatomic distance (Å) and angle (°) values and ranges: Co(1)···Co(2) 3.464(4), Co(1)–N(1,11,21) 1.945(4)–1.955(4), Co(1)–N(2,12,22) 1.881(4)–1.905(4), Co(2)–O 2.077(3)–2.127(3), *trans* N–Co(1)–N 169.1(2)–173.8(2), *cis* N–Co(1)–N 82.4(2)–95.2(2), *trans* O–Co(2)–O 180.0(3), *cis* O–Co(2)–O 87.3(1)–92.7(1).

Fig. 2. Molecular structure of complex $2 \cdot 0.25H_2O$ with selected atom labelling. The solvate molecule has been omitted. Selected bond lengths (Å) and angles (°): Co–N(1) 1.927(5), Co–N(2) 1.920(5), Co–N(21) 1.949(5), Co–N(22) 1.934(5), N(1)–Co–N(11) 172.7(2), N(2)–Co–N(22) 174.0(2), N(21)–Co–N(12) 174.3(2).

cobalt(II) centre, Co(2), led us to suspect that the mononuclear 1:3 cobalt(III) complex would be capable of existence. Our suspicion was both correct and incorrect. It proved correct because the desired product has, indeed, been prepared and, simultaneously, it proved incorrect because the discrete mononuclear complex that we managed to isolate is the "wrong", i.e., the *mer* (or *trans*) isomer.

Complex $[Co\{(py)C(ph)NO\}_3] \cdot 0.25H_2O$ ($2 \cdot 0.25H_2O$) was initially isolated from the reaction system that leads to 1 by excluding the PF_6^- counterions. In a more synthetically rational way, complex $2 \cdot 0.25H_2O$ was isolated from the 1:3 reaction between $Co(O_2CMe)_2 \cdot 4H_2O$ and (py)C(ph)NOH in MeCN/DMF (1:1 v/v, DMF was used to improve the quality of the crystals) under reflux for a few hours and subsequent crystallisation of the orange

product[1] by allowing the closed reaction flask to remain undisturbed at room temperature for a period of 2–3 weeks; yields as high as 70% were obtained. Single-crystal X-ray crystallography[2] reveals that complex $2 \cdot 0.25H_2O$ consists of well-separated mononuclear molecules (Fig. 2). The Co^{III} ion is coordinated by three N,N'-bidentate chelating (or 1.011 [11], Scheme 2) (py)C(ph)NO$^-$ ligands. The six-coordinate molecule is the *mer* isomer. The observed coordination mode of the ligand is interesting because the deprotonated oxygen atom remains uncoordinated. Theoretical investigations are underway to study this oddity.

In order to investigate to what extent the nature of the substituent R on the oxime carbon of 2-pyridyloximes might affect the identity of isolated Co products (and to what extent this might prove a route to new cluster types), we studied the coordination chemistry of (py)CHNOH and (py)C(Me)NOH, see Scheme 1. The Co/(py)CHNOH chemistry is almost identical with the Co/(py)C(ph)NOH chemistry. The refluxing reaction mixtures $Co(O_2CMe)_2 \cdot 4H_2O/(py)CHNOH/NaClO_4$ (1:2:1)[3] in MeOH, $CoCl_2 \cdot 6H_2O/(py)CHNOH/LiOH/NaClO_4$ (1:2:2:1)[3] in H_2O and $Co(ClO_4)_2 \cdot 6H_2O/(py)CHNOH/Me_4NOH$ (1:2:2)[3] in MeOH led (under aerobic conditions) to the clean preparation of the dark red complex $[Co_3\{(py)CHNO\}_6](ClO_4)_2$ (3)[1] in 45–60% yields. The corresponding mononuclear complex $[Co\{(py)CHNO\}_3]$ (4)[1] was prepared in a manner completely analogous to compound $2 \cdot 0.25H_2O$ in 60% yield, but using (py)CHNOH instead of (py)C(ph)NOH.

Scheme 2. The crystallographically established coordination modes of the 2-pyridyloximato ligands present in complexes 1–4 and 6, and the Harris notation [11] that describes these modes.

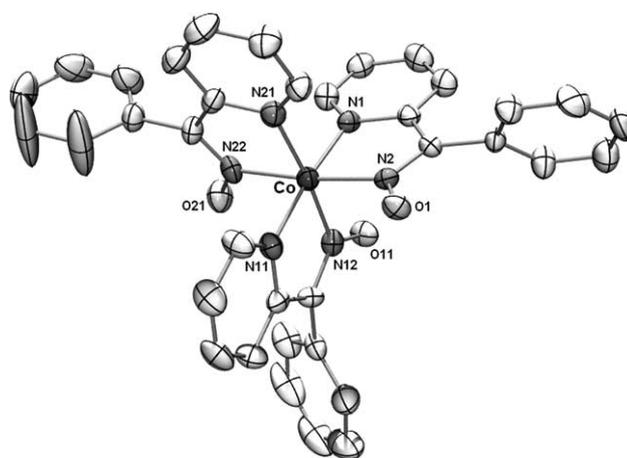[3] *Caution!* Although no such behaviour was observed during the present work, it should be mentioned that perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care and in very small quantities.

The molecular structures[2] of the cation of **3** (Fig. 3) and complex **4** are very similar with the structures of the cation of **1** · 6MeCN and complex **2** · 0.25H$_2$O, respectively; obviously, the replacement of (py)C(ph)NO$^-$ by (py)CHNO$^-$ has little structural effect. The six-coordinate molecule **4** is like **2** · 0.25H$_2$O, the *mer* isomer. As far as the symmetry elements of **3** are concerned, the central cobalt(II) ion [Co(2)] sits on a 3-fold inverse axis of symmetry, while the terminal cobalt(III) ion [Co(1)] sits on a 3-fold symmetry axis.

Complexes [Co$_3${(py)C(Me)NO}$_6$](ClO$_4$)$_2$ (**5a**)[3] and [Co$_3${(py)C(Me)NO}$_6$](PF$_6$)$_2$ (**5b**) were prepared in a manner analogous to compounds **3** and **1** · 6MeCN, respectively, in 50–60% yields. Despite our intense efforts, we could not grow crystals suitable for single-crystal X-ray crystallography. Thus, the dark red microcrystalline solids were characterised by microanalyses[1], IR, UV/Vis spectroscopies and room-temperature magnetic susceptibilities (vide infra). These studies provide strong evidence that the cations of **5a** and **5b** have completely analogous structures to those of the cations present in **1** · 6MeCN and **3**. The corresponding mononuclear, orange cobalt(III) complex was prepared from the 1:3 aerobic reaction of Co(O$_2$CMe)$_2$ · 4H$_2$O and (py)C(Me)NOH in refluxing MeNO$_2$ (this solvent was used for crystallisation purposes) and subsequent crystallisation from the resulting solution by layering with Et$_2$O/*n*-hexane (1:1, v/v). The yield was ~50%. X-ray crystallography[2] revealed the formula [Co{(py)C(Me)-NO}$_3$] · 3MeNO$_2$ (**6** · 3MeNO$_2$)[1]. We were pleased to see (somewhat to our surprise based on the experience we had with the structures of **2** · 0.25H$_2$O and **4**) that the octahedral complex is the *fac* (or *cis*) isomer (Fig. 4). The Co^{III} ion sits on a 3-fold axis of symmetry. The *fac* nature of **6** · 3MeNO$_2$ may be a consequence

Fig. 4. Molecular structure of complex **6** · 3MeNO$_2$ with selected atom labelling. The solvate molecules have been omitted. Unprimed, primed and doubly primed atoms have the symmetry operators $(-1 + x - y, 1 - y, z)$, (x, y, z) and $(1 - x, 2 - x + y, z)$, respectively. Selected bond lengths (Å) and angles (°): Co(1)–N(1,1′,1″) 1.946(2), Co(1)–N(2,2′, 2″) 1.905(2), and N(1)–Co(1)–N(2′) 176.1(1), N(1)–Co(1)–N(2) 82.7(1).

of the different solvents used for the preparation of the three mononuclear cobalt(III) complexes (MeNO$_2$ for **6** · 3MeNO$_2$ and MeCN or MeCN/DMF for the *mer* complexes **1** and **3**). To study this possibility, we have yet to crystallise **6** from MeCN or MeCN/DMF, and such efforts are currently in progress.

The two mononuclear *fac*-[Co^{III}{(py)C(Me)NO}$_3$] units can be regarded as tridentate "ligands" to the central cobalt(II) in the putative trinuclear cluster **5a**. It seemed reasonable to suspect that the latter could be obtained by the 2:1 reaction between complex **6** · 3MeNO$_2$ and the appropriate cobalt(II) starting material. This has, indeed, turned out to be the case (Eq. (1))[1]. This use of a simple metal ion complex, which has the appropriate functionality to act as a ligand for another metal ion, to obtain a polynuclear complex is a typical example of the "metal complexes as ligands" synthetic strategy.

$$2[\text{Co}\{(\text{py})\text{C(Me)NO}\}_3] \cdot 3\text{MeNO}_2 + \text{Co(ClO}_4)_2 \cdot 6\text{H}_2\text{O}$$
$$\underset{\textbf{6}\cdot\text{3MeNO}_2}{}$$

$$\xrightarrow[\text{T}]{\text{MeCN}} [\text{Co}_3\{(\text{py})\text{C(Me)NO}\}_6](\text{ClO}_4)_2 + 6\text{H}_2\text{O} + 3\text{MeNO}_2$$
$$\underset{\textbf{5a}}{}$$

$$(1)$$

Surprisingly, the "wrong", i.e., undesired, *mer* isomers **2** · 0.25H$_2$O and **4** can also be converted to the trinuclear clusters **1** and **3**, respectively, which contain the *fac*-[Co^{III}{(py)C(R)NO}$_3$] "ligands" (R = Ph, H), by

Fig. 3. Partially labelled representation of the mixed-valence(III/II/III) cation [Co$_3${(py)CHNO}$_6$]$^{2+}$ present in complex **3**. Identical numbers are used for atoms generated by symmetry. Selected bond lengths (Å) and angles (°): Co(1)–N(2) 1.899(2), Co(1)–N(1) 1.961(2), Co(2)–O(1) 2.102(2), and N(2)–Co(1)–N(2) 91.2(1), N(1)–Co(1)–N(1) 93.6(1), N(1)–Co(1)–N(2) 82.3(1), 93.5(1), 172.0(1), O(1)–Co(2)–O(1) 89.8(1), 90.2(1), 180.0(1).

their reactions with the appropriate cobalt(II) starting materials. This may suggest the occurrence of an equilibrium between *mer*- and *fac*-[Co^{III}{(py)C(R)NO}$_3$] species in solution, which shifts to the *fac* isomer upon addition of external Co^{II} [13].

Complexes $\mathbf{2} \cdot 0.25H_2O$, $\mathbf{4}$ and $\mathbf{6} \cdot 3MeNO_2$ are diamagnetic, as expected. The room-temperature, effective magnetic moment (μ_{eff}) values of $\mathbf{1}$, $\mathbf{3}$, $\mathbf{5a}$ and $\mathbf{5b}$ are 5.01, 5.13, 4.99 and 5.07 BM per trimer, respectively; these values are consistent with the presence of one high-spin Co^{II} ion with octahedral stereochemistry [12d]. The IR spectra of $\mathbf{3}$ and $\mathbf{5a}$ exhibit bands near 1100 and 625 cm^{-1}, due to the $v_3(F_2)$ and $v_4(F_2)$ modes of the uncoordinated T_d ClO$_4^-$, respectively [14]. A strong band at ~845 cm^{-1} and a medium-intensity band at 558 cm^{-1} in the IR spectra of $\mathbf{1}$ and $\mathbf{5b}$ arise [14] from the $v_3(F_{1u})[v(PF)]$ and $v_4(F_{1u})[\delta(FPF)]$ vibrations of the uncoordinated O_h PF$_6^-$ ion, respectively. Two bands, one medium to strong at 1606–1598 cm^{-1} and one of variable intensity at 1244–1222 cm^{-1}, are common in the spectra of $\mathbf{1}$–$\mathbf{4}$, $\mathbf{5a}$, $\mathbf{5b}$ and $\mathbf{6} \cdot 3MeNO_2$; these bands are assigned [15] to the oximate $v(C=N)$ and $v(N–O)$ modes, respectively, although the higher-wavenumber band may also have an aromatic stretch character. The $v(N–O)$ mode is situated at a lower wavenumber in the spectra of the trinuclear clusters than for their corresponding mononuclear, "ligand" cobalt(III) complexes; for example, the $v(N–O)$ band appears at 1232 and 1244 cm^{-1} in $\mathbf{3}$ and $\mathbf{4}$, respectively. This shift is consistent with the oximato O-coordination in the trinuclear complexes. The solid-state (diffuse reflectance) UV/Vis spectra of $\mathbf{2} \cdot 0.25H_2O$, $\mathbf{4}$ and $\mathbf{6} \cdot 3MeNO_2$ are typical for low-spin Co^{III}N$_6$ chromophores [16]. The low-spin octahedral ground term is $^1A_{1g}$ and there are two relatively low lying spin allowed transitions, with lower lying spin triplet partners, all derived from $(t_{2g}^5)(e_g)$. Under this scheme, the bands in the spectrum of $\mathbf{6} \cdot 3MeNO_2$, for example, at 29.13, 21.35, 17.10 and 13.36 kK are assigned [16] to the $^1A_{1g} \rightarrow {}^1T_{2g}, {}^1T_{1g}, {}^3T_{2g}$ and $^3T_{1g}$ transitions, respectively. The spectra of the trinuclear Co^{III}Co^{II}Co^{III} clusters exhibit bands at approximately the same energies with those of their corresponding mononuclear Co^{III} complexes, and maxima characteristic of Co^{II}O$_6$ chromophores [16]. For example, the spectrum of $\mathbf{5a}$ shows bands/shoulders at 29.27, 21.55, 17.50 and 13.00 kK due to its *fac*-[Co^{III} {(py)C(Me)NO}$_3$] units (and assigned as above), and additional bands at 19.23 and 15.80 kK due to its high-spin octahedral Co^{II}(O$_{oximato}$)$_6$ unit and assigned (under O_h symmetry) to the $^4T_{1g} \rightarrow {}^4T_{1g}(P), {}^4A_{2g}$ transitions, respectively [16].

In conclusion, the present work emphasises the ability of the anionic 2-pyridyl oximes to form new structural types in Co chemistry. The general novel structure of compounds [Co$_3${(py)C(R)NO}$_6$]$^{2+}$ (R= H, Me, Ph) is distinctly different from those recently reported [7] with (py)$_2$CNO$^-$ (Scheme 1), emphasising the dependence of the product identity on relatively small changes in the 2-pyridyloxime ligand employed. Although the basic synthetic routes established for decades have remained as entry points into Co chemistry at the beginning of the 21st century, the application of these routes with a wider range of ligands expands the "possible" and encompasses some of the (at least previously considered) "non-existent" [6a]. We believe that the preliminary results of the present work are good examples of this statement.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, on quoting the deposition numbers CCDC 264165 ($\mathbf{1} \cdot 6MeCN$), 264166 ($\mathbf{2} \cdot 0.25H_2O$), 264167 ($\mathbf{3}$), 264168 ($\mathbf{4}$) and 264169 ($\mathbf{6} \cdot 3MeNO_2$) (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement

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[13] NMR studies of such equilibria and isomerization processes, as well as equilibria between Co^{III} and $Co^{III}Co^{II}Co^{III}$ species, will be reported in the full paper, Inorg. Chim. Acta, to be submitted.

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