Synthesis and characterisation of bis(β-ketoaminato) complexes of cobalt(II)†

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Received 21st October 2009, Accepted 6th January 2010
First published as an Advance Article on the web 27th January 2010
DOI: 10.1039/b921153e

Condensation of 1-phenyl-1,3-butanedione with various substituted anilines affords N-aryl substituted β-ketoamines PhC(O)CHC(CH_3)Naryl, which, when deprotonated and reacted with $Co(OAc)_2 \cdot 4H_2O$ yields a series of bis(β-ketoaminato)cobalt(II) complexes **1b** to **6b** (aryl = Ph, **1b**; *p*-$CH_3C_6H_4$, **2b**; 2,6-$(CH_3)_2C_6H_3$, **3b**; 3,5-$(CH_3)_2C_6H_3$, **4b**; *p*-$CF_3C_6H_4$, **5b**; *p*-$CH_3OC_6H_4$, **6b**). All six cobalt compounds were characterised by ^{1}H NMR, elemental analysis, magnetic susceptibility, and X-ray crystallography, indicating a uniform tetrahedral geometry in all cases. Electrochemical oxidation potentials indicate sensitivity to aryl substitution at the *ortho*- and *para*- positions, but not to *meta*-substitution, a conclusion supported by DFT calculations.

Introduction

Increasing attention is being focused on the development of catalysts based on first-row transition metals, in part because relative to their second- and third-row counterparts they are less expensive, less toxic, and cause less harmful environmental impacts.[1] An emerging realization is that the distinction extends to characteristic reactivity, with one-electron processes and radical intermediates playing a more prominent role in their catalytic activity.[2] Indeed, first-row metals are those most commonly associated with metalloenzyme-directed biological catalysis, for which radical mechanisms are commonplace.[3] In this regard, the well established radical reactivity of cobalt compounds is the basis for their catalytic behaviour toward numerous alkene addition,[4] cross-coupling[5] and other carbon-carbon bond forming reactions.[6] In particular, the ability of cobalt reagents to control the radical polymerization of functionalized alkenes, termed "cobalt-mediated radical polymerization", is a noteworthy process in which the reversible homolysis of a cobalt carbon bond is the critical factor.[7] The one-electron reactions in all these chemistries are proposed to involve the Co(II)/Co(III) couple, a parameter known to be sensitive to the geometry and corresponding spin-state of the cobalt species involved, which in turn is necessarily controlled by the ligands bound to the metal centre. For example, an elegant study by Lippard showed that in a series of Co(II) complexes bearing tetradentate tropocoronand ligands of variable ring size, only small rings could enforce a low-spin square-planar arrangement, and that as the macrocyclic ligand was expanded to include increasing numbers of methylene groups, the system gradually adopted an electronically more favoured high-spin tetrahedral geometry.[8] It was shown that this gradual shift in the dihedral twist angle among the four donor atoms correlated smoothly with the Co(II)/Co(III) redox couple.[9]

Few of the catalytic systems noted previously involve well-defined cobalt complexes in which systematic variation of the ligand properties has been undertaken, though one recent study demonstrates the importance of ligand electronic effects: $Co(acac)_2$ and $Co(acac\text{-}F_3)_2$ controls the radical polymerisation of vinyl acetate, but $Co(acac\text{-}F_6)_2$ does not.[10] In particular, we are interested in an examination of ligand effects on the Co(II) oxidation potential and its impact on catalytically-relevant reactivity. In this regard, β-ketoaminate ligands,[11] like many other Schiff base systems,[12] are particularly attractive scaffolds for such an investigation, due the wide range of commercially available anilines that may be used in the facile preparation of the proligands. This in turn can be used to present a finely-tuned diversity of both steric and electronic properties in the resulting metal complexes, given the proximity of the N-aryl group to the metal centre. Here we describe a series of six bis(β-ketoaminato)cobalt(II) complexes encompassing both steric and electronic variation in the N-substituted aryl groups (Scheme 1), including electrochemical and structural characterization of all compounds.[13] Our principal interest in such compounds is to develop their use as well defined mediators for cobalt-mediated radical polymerisation (CMRP), given the striking potential of cobalt complexes to direct the polymerisation of monomers normally difficult to control by other means.[2a] Our preparation of three of these complexes (**1b**, **3b**, and **6b**) has been recently described,[14] along with experiments showing that the rate of radical-initiated vinyl acetate polymerisation changes dramatically depending on the both the steric and electronic profile of the substituted aryl group.

Results and discussion

The condensation of 1-phenyl-1,3-butanedione with various substituted anilines affords N-aryl substituted β-ketoamine compounds **1a** to **6a**. Reaction of deprotonated β-ketoamines with $Co(OAc)_2 \cdot 4H_2O$ in heated methanol results in the rapid precipitation of bis(β-ketoaminato)cobalt(II) complexes **1b** to **6b** as

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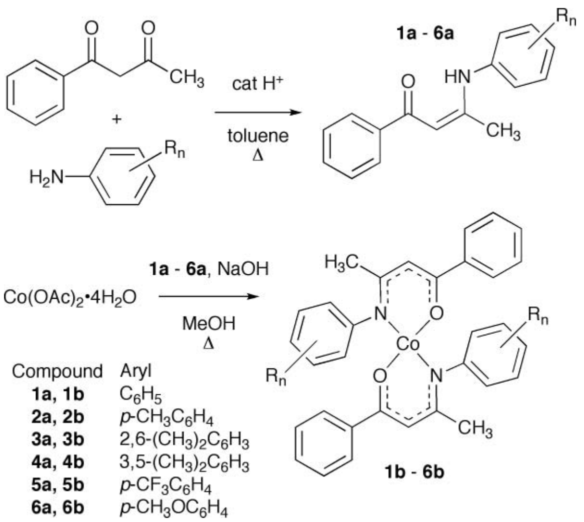
† Electronic supplementary information (ESI) available: Experimental data for X-ray structure determination of **1b** to **6b**, DFT optimised metrical parameters and thermochemical data for **1c**, **5c**, and **6c** (19 pages). CCDC reference numbers 752052, 752053, 752054, 752055 and 752056. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b921153e



Scheme 1 Synthesis and number scheme for β-ketoamine and bis(β-ketoaminato)cobalt(II) complexes.

red-orange microcrystalline solids (Scheme 1) in moderate to high (61 to 84%) yields, with the exception of lower yields for **6b**. The compounds dissolve in polar solvents such as CH_2Cl_2 and THF to form air-sensitive red solutions, but they are air-stable for short periods as solids, allowing them to be easily prepared in air. However, noticeable decomposition occurs over a period of weeks or months. Analytically pure and X-ray quality samples may be obtained by recrystallization from CH_2Cl_2/hexanes under inert atmosphere.

The bis(β-ketoaminato) species exhibit solution-phase magnetic moments in the range 4.0 to 4.5 μ_B, consistent with the high-spin d^7 $S = {}^3/_2$ configuration expected for Co(II) in a tetrahedral geometry.[15] The ^{1}H NMR spectra exhibit well-defined paramagnetically shifted and broadened peaks with accurate integrations. Chemical shifts due to similar proton environments are consistent across the series of compounds, which permits assignment of all peaks in the spectra (Table 1). Their similarity is further evidence of a consistent tetrahedral geometry in solution.

The aromatic signals of the ligand backbone phenyl group occur as three signals consistently at around +19, +14, and +10 ppm, while the backbone methyl and methine protons yield signals near −20 and −33 ppm, respectively. The aromatic protons on the N-substituted aryl group occur at approximately +12 (*meta*), −26 (*para*), and −50 (*ortho*) ppm. The far greater paramagnetic shift and broadening observed for the *ortho*- and *para*-hydrogens suggests greater electronic communication of these positions with the metal centre, consistent with the observation that the redox potential of the complexes is sensitive to variation of *ortho*- and *para*-groups (*vide infra*). The signals due to the various substitutions appear at unique locations: +27.1 ppm for the *para*-CH_3 in **2b**, +3.3 ppm for the *ortho*-CH_3 groups in **3b**, −11.5 ppm, for the *meta*-CH_3 groups in **4b**, and +3.4 for the *para*-CH_3O group in **6b**.

Table 1 Chemical shift values (ppm) for ^{1}H NMR spectra of compounds **1b** to **6b**

	1b	2b	3b	4b	5b	6b
p-CH_3		27.1				
C_6H_5 *o* or *m*-H	19.4	19.0	17.3	19.0	20.1	19.2
C_6H_5 *p*-H	14.8	14.7	14.3	14.5	15.3	14.8
aryl *m*-H	12.8	12.6	11.2		13.5	11.9
C_6H_5 *o* or *m*-H	10.1	10.0	9.6	10.0	10.3	10.0
o-CH_3			3.3			
p-CH_3O						3.4
m-CH_3				−11.5		
CH_3	−21.3	−20.6	−16.4	−20.4	−23.6	−21.2
aryl *p*-H	−26.9		−25.8	−26.6		
CH	−33.2	−32.6	−34.5	−32.8	−35.2	−32.5
aryl *o*-H	−49.8	−50.1		−50.3	−50.2	−50.6

The solid-state molecular structures of all six compounds have been determined. The structures of compounds **2b**, **3b**, **4b**, and **6b** are shown in Fig. 1 to Fig. 4. Structure and refinement data are listed in Table 2, and selected metrical parameters are found in Table 3. All six compounds exhibit a similar near-tetrahedral geometry and effective C_2 symmetry. The chelate bite angles N1-Co1-O1 or N2-Co1-O2 range from 95.13(4)° in **3b** to 97.28(7)° in **5b**, with necessarily wider interligand angles ranging from 112.11(6)° for N2-Co1-O2 in **2b** to 124.49(8)° for N1-Co1-N2 in **4b**. The twist angles between planes, as defined by the N–Co–O angle for each chelate, range from near-perpendicular for **6b** (89.5°) to slightly flattened for **4b** (80.0°), with the other angles falling between 84° to 87°. There is therefore little or no deviation from a tetrahedral geometry beyond that dictated by a < 100°

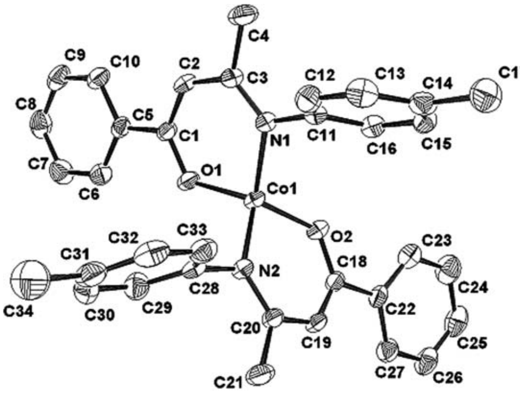


Fig. 1 Molecular structure of **2b**.

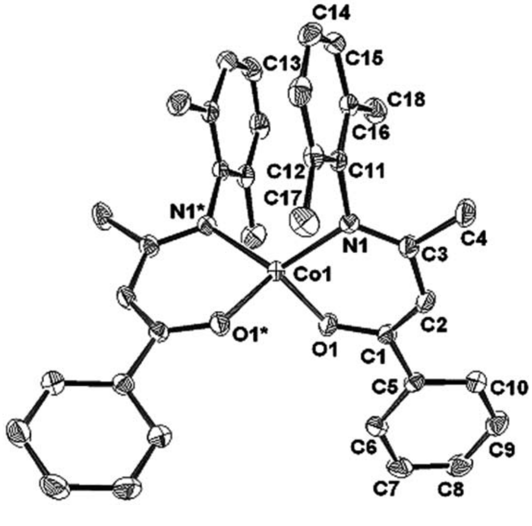


Fig. 2 Molecular structure of **3b**.

Table 2 Crystallographic structure and refinement data for compounds **1b** to **6b**

Compound	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**
Formula	$C_{32}H_{28}N_2O_2Co$	$C_{34}H_{32}N_2O_2Co$	$C_{36}H_{36}N_2O_2Co$	$C_{36}H_{36}N_2O_2Co$	$C_{34}H_{26}N_2O_2F_6Co$	$C_{34}H_{32}N_2O_4Co$
M	531.49	559.55	587.60	587.60	667.50	591.55
colour, habit	red plate	red prism	orange rod	red prism	red irregular	red irregular
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$C2/c$	$C2/c$	$C2/c$	$P2_1/c$
a/Å	9.2635(4)	10.288(2)	17.3396(5)	13.717(3)	19.808(3)	13.4825(19)
b/Å	17.9930(9)	21.067(5)	10.5700(3)	17.402(3)	10.573(1)	18.294(3)
c/Å	16.2751(9)	13.552(3)	16.4542(5)	13.486(3)	30.606(4)	11.7696(17)
α (°)	90.0	90.0	90.0	90.0	90.0	90.0
β (°)	97.640(2)	103.505(6)	92.286(1)	113.83(1)	100.456(4)	100.231(6)
γ (°)	90.0	90.0	90.0	90.0	90.0	90.0
U/Å^3	2688.6(2)	2856(1)	3013.3(2)	2944(1)	6303(2)	2856.8(7)
Z	4	4	4	4	8	4
ρ_c/g cm^{-3}	1.313	1.301	1.295	1.325	1.407	1.375
T/K	173	173	173	173	173	173
F_{000}	1108.00	1172.00	1236.00	1236.00	2728.00	1236.00
λ(Mo-Kα)/Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
μ(Mo-Kα)/cm^{-1}	6.69	6.34	6.04	6.18	6.13	6.43
Reflections Measured	16566	30714	15483	23369	31180	19915
Unique Reflections	3495	6835	3588	3586	7546	5051
R_{int}	0.072	0.036	0.032	0.044	0.041	0.066
R(F) [$I > 2\sigma(I)$]	0.045	0.035	0.031	0.035	0.044	0.053
R_w(F)	0.093	0.084	0.075	0.087	0.102	0.132
GoF	1.00	1.05	1.03	1.04	0.99	1.07

Table 3 Selected bond distances (Å) and angles (°) for compounds **1b** to **6b**

Compound	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**
aryl	C_6H_5	p-$CH_3C_6H_4$	2,6-$Me_2C_6H_3$	3,5-$Me_2C_6H_3$	p-$C_6H_4CF_3$	p-$C_6H_4OCH_3$
Co1-O1	1.917(3)	1.9197(12)	1.9306(10)	1.9096(12)	1.9156(16)	1.931(3)
Co1-O2	1.914(3)	1.9341(12)			1.9067(15)	1.927(3)
Co1-N1	1.951(3)	1.9702(14)	1.9855(11)	1.9459(14)	1.9642(19)	1.964(3)
Co1-N2	1.958(3)	1.9640(14)			1.9654(18)	1.967(3)
N1-arylC	1.433(5)	1.429(2)	1.4381(18)	1.424(2)	1.425(3)	1.438(5)
N2-arylC	1.437(5)	1.434(2)			1.423(3)	1.432(5)
N1-Co1-O1	96.30(12)	96.57(6)	95.13(4)	95.98(5)	97.28(7)	95.90(12)
N2-Co1-O2	97.16(13)	96.42(6)			95.81(7)	96.66(12)
N1-Co1-O2	117.31(12)	116.60(6)	119.10(5)	110.59(6)	117.15(8)	114.57(13)
N2-Co1-O1	119.22(13)	112.11(6)			122.70(7)	118.79(12)
O1-Co-O2	112.92(11)	118.19(6)	109.19(7)	121.40(8)	114.57(7)	113.53(12)
N1-Co-N2	115.35(13)	118.37(6)	120.41(7)	124.49(8)	110.76(8)	118.66(13)
chelate twist	86.67	86.75	85.95	80.02	84.23	89.50

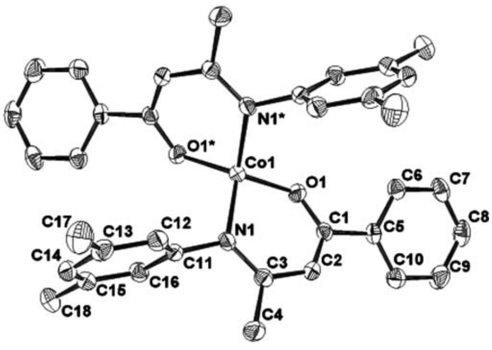


Fig. 3 Molecular structure of **4b**.

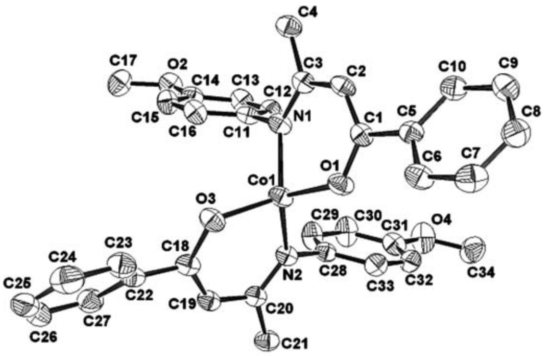


Fig. 4 Molecular structure of **6b**.

chelate bite angle. The ketoaminato ligand rings are all nearly planar, except in the case of **3b**, in which the two N-aryl groups are within 5° of perfect coplanarity, and one *ortho*-methyl group of each aryl moiety is positioned over the centre of the other N-aryl ring (Fig. 5). As a result, the closest contact between an *ortho*-carbon and the other aryl ring plane is 3.35 Å, and that

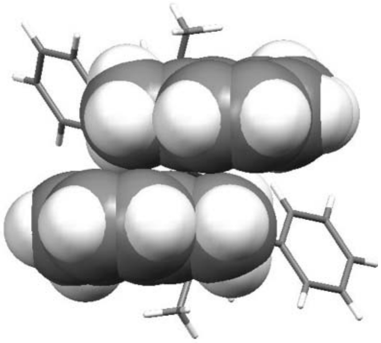


Fig. 5 Partial space filling model of **3b**, illustrating the coplanarity of close proximity of the 2,6-$(CH_3)_2C_6H_3$ rings.

between a methyl hydrogen and the aryl ring plane is 2.71 Å, effectively bringing the rings well within van der Waals contact. In order to position the aryl rings in this way, the ketoaminato-Co ring is distorted, so that each OCCCN plane moves toward the second nitrogen atom, and the Co lies 0.38 Å out of this plane. We ascribe this distortion to electronic π-stacking and $CH_3 \cdots$ aryl ring quadrupolar interactions in the solid state. There is nothing anomalous about the ^1H NMR signals of **3b**, so we do not believe that this interaction is maintained in solution.

The consistent tetrahedral geometry within this series of complexes corresponds to that observed for other bis(β-ketoaminato) cobalt compounds,[15] but stands in contrast with the variation exhibited by both bis(β-ketoaminato) complexes of nickel[16] and recently described bis(iminopyrollyl)cobalt(II) species.[17] In the latter case, a sterically-driven square planar and low-spin $S = \frac{1}{2}$ configuration for cobalt may be adopted, but there is only a very small energetic stability for the square planar arrangement.[17] Unlike recently reported square planar cobalt complexes bearing redox non-innocent aminophenolate or *o*-phenylenediamine groups, which are best described as Co(III) with a delocalized combination of one mono- and one dianionic ligand,[18] comparison of the β-ketoaminato ligands in these compounds to those observed in structurally characterized Ni(II)[19] and Co(III)[20] complexes reveals no structural evidence for a similar ligand redox particpation, one that would require antiferromagnetic coupling of a $S = \frac{1}{2}$ radical dianionic ligand to a highly unusual tetrahedral $S = 2$ Co(III). We are therefore confident in assigning the oxidation state of these compounds unambiguously as Co(II).

Given the key role of the Co(II)/Co(III) redox couple to the single-electron catalysis of cobalt compounds, compounds **1b** to **6b** were studied by cyclic voltammetry in CH_2Cl_2. The shared tetrahedral geometry means that any observed variation in redox potentials across this series can only be attributed to electronic effects of the aryl group substitutions. No reduction features are observed for any of the complexes up to ~ −1.2 V *vs.* SCE. A single irreversible oxidation feature is observed for **1b**, **2b**, and **5b**, while a slightly quasi-reversible oxidation is seen for **3b**, **4b**, and **6b**. Current-peak potentials for these oxidations are shown in Table 4. For the four compounds with a single *para*-substituent on the aryl ring, a plot of electrochemical oxidation potential *vs.* Hammett parameter σ^{+}[21] yields a linear correlation (Fig. 6), consistent with increasing positive charge at the metal centre upon oxidation to cobalt(III), and suggesting a formal resonance contribution of the *para*-group in addition to simple inductive effects. This suggestion is borne out by the differences observed in the oxidation potentials of the two xylyl derivatives: the 2,6-$(CH_3)_2C_6H_3$ aryl group results in a far lower oxidation potential than that caused by 3,5-$(CH_3)_2C_6H_3$, which in turn exhibits a relatively slight difference compared to that of the complex bearing unsubstituted phenyl groups. Only substitutions at the *ortho*- and *para*- positions of the phenyl rings are in formal resonance with the nitrogen atom (and so with the cobalt centre), while substitution of the *meta* positions has little or no electronic effect.

Table 4 Electrochemical oxidation potentials of compounds **1b** to **6b** in CH_2Cl_2

Compound	aryl	$E_{p,a}$ *vs.* SCE/mV
6b	*p*-$CH_3OC_6H_4$	883
3b	2,6-$(CH_3)_2C_6H_3$	905
2b	*p*-$CH_3C_6H_4$	955
4b	3,5-$(CH_3)_2C_6H_3$	1002
1b	C_6H_5	1021
5b	*p*-$CF_3C_6H_4$	1106

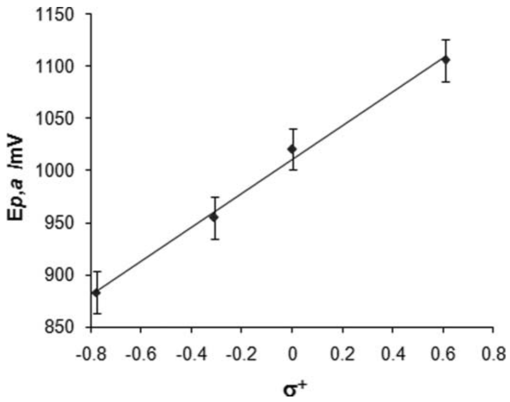


Fig. 6 Variation of electrochemical oxidation potential *vs.* SCE with Hammett parameter σ^{+} for **1b**, **2b**, **5b**, and **6b**.

These conclusions are supported by theoretical calculations on these complexes. DFT optimisations were performed on structures **1c**, **5c**, and **6c**, simplified model versions of complexes **1b**, **5b**, and **6b** respectively in which the ligand backbone phenyl group has been replaced with a methyl substituent. These optimisations accurately reproduce the observed tetrahedral geometries and give reasonable agreements for experimental bond lengths and angles. As expected for a d^7 tetrahedral complex, the singly-occupied HOMO of **1c** has cobalt d-orbital character and is effectively σ* antibonding with respect to orbital contributions from all four ligand donor atoms (Fig. 7A). The calculated energies of the HOMO vary as expected with the *para*-substitution, so that the more electron-donating the aryl moiety, the higher-energy the HOMO and the more accessible the electron becomes: **5c** −6.01 eV, **1c** −5.42 eV, **6c** −5.22 eV. As well, closer examination of the HOMO distribution over the β-ketoaminato ligand in **1c** (Fig. 7B) shows the expected contributions from the aryl ring, with considerable contribution to the HOMO from the p-orbitals of the *ortho*- and *para*- aryl carbons, but little or no meaningful contribution from the *meta*-carbons, in keeping with the lack of sensitivity of the redox potential to *meta*-substitution.[22]

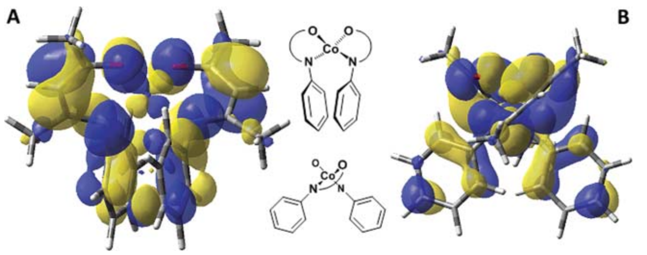


Fig. 7 Views of the HOMO of **1c**, illustrating the metal d-orbital contribution (A) and the contributions from the aromatic ring (B).

These results provide useful insight into the ligand substitutions necessary to make effective changes to the steric and electronic properties at the cobalt centre, which will guide further efforts to improve their use as effective and well-defined mediators for CMRP. Such studies are currently in progress.

Experimental

Materials

Hexanes (ACS, Fisher), dichloromethane (HPLC, Fisher), diethylether (anhydrous, VWR), and tetrahydrofuran (HPLC, Fisher) were purified in Glass Contour solvent purification towers.[23] Methanol (ACS, Fisher) and toluene (ACS, Fisher) was used as received. $CDCl_3$ (99.6+ atom% D) was dried over P_2O_5, distilled under reduced pressure, freeze-pump-thaw degassed, and stored under dinitrogen. 1-Phenyl-1,3-butanedione (99%, Aldrich), *p*-toluidine (99%, Aldrich), 3,5-dimethylaniline (99%, Aldrich), *p*-anisidine (99%, Aldrich), KOH (>90%, Aldrich), and $Co(OAc)_2{\cdot}4H_2O$ (>98%, Aldrich) were used as received.

Characterization

^1H NMR data were collected on a Varian 400 MHz NMR spectrometer at room temperature, in J. Young valve NMR tubes in $CDCl_3$. Chemical shift values were calibrated relative to residual $CHCl_3$, taken as 7.24 ppm. Magnetic moments were determined either in $CDCl_3$ solution by Evans' method[24] or in the solid state on powdered samples using a Johnson-Matthey magnetic susceptibility balance; standard diamagnetic corrections were applied.[25] Elemental analyses were determined with a Carlo Erba Elemental Analyzer EA 1108 at the University of British Columbia. Cyclic voltammetry was performed with a EG&G Princeton Applied Research model 263A potentiostat using ~4 mM solutions in anhydrous anaerobic CH_2Cl_2 with 0.1 M nBu_4NClO_4. A glassy carbon disk working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl pseudoreference electrode were employed. The scan rate was 100 mV s^{-1} and results are reported relative to the saturated calomel electrode (SCE), as measured against internal ferrocene standards, taken as +480 mV *vs.* SCE under these conditions.[26]

Computational details

All theoretical calculations were performed using Gaussian03W[27] utilizing the LANL2DZ basis set and a DFT method using the three-parameter exchange functional of Becke[28] and the correlation functional of Lee, Yang, and Parr (B3LYP).[29] The LANL2DZ basis set includes both Dunning and Hay's D95 sets for H, C, N, O, and F[30] and the relativistic electron core potential (ECP) sets of Hay and Wadt for Co.[31] Geometry optimizations were performed in C_1 symmetry, and frequency calculations on optimized geometries established the absence of any imaginary frequencies. The values of $<S^2>$ indicated only minor spin contamination. DFT optimised structures and thermochemical data are provided as Electronic Supplementary Information.

X-ray structure determination

Crystal and structure refinement data for the structure determination of **1b** to **6b** is listed in Table 2. Full details of crystal structure determination and corresponding data are provided as Electronic Supplementary Information.

Synthesis

General considerations. Syntheses of the β-ketoamine proligands and all cobalt complexes was carried out under air. All subsequent manipulations and characterizations were carried out in an inert atmosphere glove box or on a vacuum/nitrogen line using standard air-sensitive Schlenk techniques unless otherwise noted. All β-ketoamine proligands were prepared *via* condensation of 1-phenyl-1,3-butanedione with the appropriate anilines in refluxing toluene in a Dean–Stark apparatus, using a catalytic amount of *p*-toluenesulfonic acid.[32] Syntheses of the bis(β-ketoaminato)cobalt(II) complexes is an improved modification of that described for complexes **2b** and **3b**. Our preparations of **1b**, **3b**, and **5b**, have been described previously.[14]

Synthesis of $Co(PhC(O)CHC(CH_3)NC_6H_4\text{-}p\text{-}CH_3)_2$ (2b). $Co(OAc)_2{\cdot}4H_2O$ (0.317 g, 1.27 mmol) was dissolved and heated in a minimal amount of MeOH. *N*-*p*-tolyl β-ketoamine **2a** (0.528 g, 2.10 mmol) was added to the solution to give a suspension. KOH (0.145 g, 2.58 mmol) was dissolved in MeOH (2 mL) and added dropwise to the stirred reaction solution, resulting in the precipitation of an orange solid, collected by filtration through a crucible and washed with cold MeOH (5 mL) to yield 0.403 g (68% yield) of **2b**. The orange solid was recrystallised from CH_2Cl_2 layered with hexanes to afford X-ray quality crystals as deep red blocks.

Elemental analysis found: C 73.28, H 5.82, N 5.10; calc. for $C_{34}H_{32}N_2O_2Co$: C 73.00; H 5.76; N 5.01. ^1H HMR (*δ*): 27.06 (3H), 19.05 (2H), 14.69 (1H), 12.60 (2H), 9.99 (2H), −20.64 (3H), −32.58 (1H), −50.10 (2H). Magnetic moment $\mu = 4.2\ \mu_B$.

Synthesis of $Co(PhC(O)CHC(CH_3)NC_6H_3\text{-}3,5\text{-}(CH_3)_2)_2$ (4b). *N*-3,5-xylyl β-ketoamine **4a** (1.53 g, 6.12 mmol) was dissolved and heated in MeOH (25 mL). KOH (0.355 g, 6.32 mmol) was dissolved in MeOH (4 mL) and added dropwise to the stirred reaction solution. $Co(OAc)_2{\cdot}4H_2O$ (0.776 g, 3.12 mmol) was added to the solution, resulting in the formation of an orange precipitate, which was collected by filtration to yield 1.53 g (84% yield) of **4b**. The orange solid was recrystallized from CH_2Cl_2 to afford X-ray quality crystals as deep red blocks.

Elemental analysis found: C 73.58, H 6.20, N 4.77; calc. for $C_{36}H_{36}N_2O_2Co$: C 73.58, H 6.18, N 4.77. ^1H NMR (*δ*) 19.02 (2H), 14.51 (1H), 10.0 (2H), −11.5 (6H), −20.35 (3H), −26.61 (1H), −32.76 (1H), −50.30 (2H). Magnetic moment $\mu = 4.4\ \mu_B$.

Synthesis of $Co(PhC(O)CHC(CH_3)NC_6H_4$-*p*-$OCH_3)_2$ (6b). $Co(OAc)_2{\cdot}4H_2O$ (1.87 g, 7.50 mmol) was dissolved and heated in 10 mL MeOH. *N*-*p*-anisyl β-ketoamine **6a** (4.01 g, 15.0 mmol) was added to the stirred reaction solution to give a suspension. KOH (0.846 g 15.1 mmol) was dissolved in MeOH (8 mL) and added dropwise to the stirred reaction solution over 5 min. The solution first turned green, but after 5 min generated an orange precipitate that was collected by filtration to yield 1.25 g (28% yield) of **6b**. The orange solid was recrystallised from CH_2Cl_2 layered with hexanes to afford X-ray quality crystals as deep red needles.

Elemental analysis found: C 69.03, H 5.51, N 4.99; calc. for $C_{34}H_{32}N_2O_2Co$: C 69.03, H 5.45, N 4.74. ^1H NMR (δ) 19.21 (2H), 14.76 (1H), 11.85 (1H), 10.02 (2H), 3.35 (3H), −21.20 (3H), −32.49 (1H), −50.56 (2H). Magnetic moment $\mu = 4.5\ \mu_B$.

Conclusions

A series of bis(β-ketoaminato)cobalt(II) complexes was prepared, bearing various substituents on the N-bound aryl rings. All compounds exhibited tetrahedral geometry as determined by X-ray crystallography, and as consistent with their magnetic susceptibilities and ^1H NMR spectra. The electrochemical oxidation potentials were found to be sensitive to variation in *ortho*- and *para*- substitution on the N-bound aryl rings, consistent with a significant contribution to each compound's HOMO from the corresponding carbon atoms as determined by DFT calculations.

Acknowledgements

We thank Dr. Yun Ling of The University of British Columbia for elemental analyses, and both NSERC of Canada and UBC Okanagan for funding.

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