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• CHIJEuropean Journal • of Inorganic Chemistry

DOI:10.1002/ejic.201402895

# Influence of Ligand Substitution Pattern on Structure in Cobalt(II) Complexes of Bulky *N*,*N*'-Diarylformamidinate *N*-Oxides

Mihaela Cibian,<sup>[a]</sup> Sophie Langis-Barsetti,<sup>[a]</sup> Fernanda Gomes De Mendonça,<sup>[a]</sup> Sammy Touaibia,<sup>[a]</sup> Sofia Derossi,<sup>[a]</sup> Denis Spasyuk,<sup>[a]</sup> and Garry S. Hanan<sup>\*[a]</sup>

Keywords: Cobalt / N,O ligands / Substituent effects / Structure elucidation / Stereochemistry

Cobalt(II) complexes of bulky *N*,*N*'-diarylformamidinate *N*-oxide ligands were synthesized and structurally characterized. The cobalt(II) bis(chelates) are square-planar (low spin) in the solid state, according to XRD and magnetic measurements ( $\mu_{\rm eff} = 1.8$  to 2.1  $\mu_{\rm B}$ ), but show square-planar (low spin) to tetrahedral (high spin:  $\mu_{\rm eff} = 3.5$  to 4.7  $\mu_{\rm B}$ ) isomeriza-

tion in solutions of noncoordinating solvents, as demonstrated by different spectroscopic techniques. The isomerization equilibrium is highly sensitive to the substitution pattern on the ligand due to a combination of steric and electronic influences.

## Introduction

Several reports related to amidine N-oxide (AMOX, also called a-aminonitrones and N-hydroxyamidines) ligands and their transition metal complexes exist in the literature.<sup>[1]</sup> However, investigation of their properties from a coordination and supramolecular chemistry perspective has received little attention. Amidinate ligands are closely related to the N-hydroxyamidinate ligands and have been intensively explored in organometallic and coordination chemistry over the past decades, resulting in applications in catalysis and materials.<sup>[2]</sup> AMOX ligands are good chelators for metal ions and exhibit good electronic delocalization in the amidine backbone. Furthermore, they offer the possibility for modulation and fine-tuning of their electronic and steric properties by varying the substitution pattern on the three atoms of the amidine moiety.<sup>[1a,1d]</sup> Our goal is to fine-tune the properties of their corresponding metal complexes for applications in catalysis and magnetic materials.

Our preliminary results regarding the  $Co^{II}L_2$  complex (2a) (Scheme 1), where HL = *N*-hydroxy-*N*,*N'*-bis(2,6-dimethylphenyl)formamidine (1a), highlight an interesting consequence of the metalligand interaction: steric and electronic effects combine to offer a rare square-planar geometry around the d<sup>7</sup> Co<sup>II</sup> centre in a bis(bidentate) environment, while permitting facile oxidation of the metal ion.<sup>[3]</sup> In solutions of noncoordinating solvents, a square-planar to tetrahedral isomerisation can be observed. For a tetracoordinate cobalt(II) system this is particularly interesting, because the structural change is also accompanied by a change in spin.<sup>[4]</sup> Investigation of such systems affords detailed information concerning their coordination number and geometry, which is needed to predict and control the architecture and properties of the transition-metal complexes for application purposes.<sup>[5]</sup>



Scheme 1. Synthesis of Co(AMOX)<sub>2</sub> complexes 2a-c.

The square-planar to tetrahedral isomerisation of a series of bis(chelate) metal(II) compounds was previously studied by Holm.<sup>[5a,6]</sup> In cobalt-based systems, this process was investigated for organometallic complexes,<sup>[7]</sup> and for cobalt complexes of triazene 1-oxides,<sup>[8]</sup> tropocoronand macrocycles<sup>[9]</sup> and iminopyrrolyl ligands.<sup>[10]</sup> These studies revealed the importance of the electronic and steric properties of the ligand on the structural preference of the complex. Recently, the same type of processes was also reported for cobalt complexes of a-imino alkoxide ligands.<sup>[11]</sup> However, examples of square-planar to tetrahedral isomerisation in

<sup>[</sup>a] Département de Chimie, Université de Montréal,

<sup>2900</sup> Edouard-Montpetit, Montréal, Québec, H3T-1J4, Canada E-mail: garry.hanan@umontreal.ca http://www.groupeenergieverte.com/

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201402895.

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five-membered ring metal complexes of N,O-bidentate ligands are scarce.<sup>[5a,8,11,12]</sup>

The cobalt bis(chelates) of sterically demanding AMOX ligands offer a new opportunity to explore the effect of ligand-metal interactions on their structural, spectroscopic and electrochemical properties. Homoleptic complexes of cobalt(II) (**2b**-**c**; Scheme 1) with the following AMOX ligands: *N*-hydroxy-*N*,*N'*-bis(2,6-diisopropylphenyl)formamidine (**1b**) and *N*-hydroxy-*N*,*N'*-bis(2-isopropylphenyl)-formamidine (**1c**) were synthesised and characterised.

# **Results and Discussion**

## Synthesis

The syntheses of ligands **1a–c** and complex **2a** were previously reported.<sup>[3,13]</sup> Complexes **2b** and **2c** were also straightforward to prepare by treating 2 equiv. of the corresponding ligand with cobalt(II) acetate in aqueous ethanol at room temperature. A green precipitate formed in each case, and the products were isolated in good yields (81– 90%) as air-stable powders (Scheme 1). The solids are airstable for months without decomposition and readily dissolve in chlorinated solvents to give yellow-orange solutions, but are poorly soluble in polar solvents. The compounds undergo oxidation over a period of days when left in solution. Complexes **2a**–c were characterised by X-ray crystallography, <sup>1</sup>H NMR and UV/Vis spectroscopy, mass spectrometry and elemental analysis.

#### **X-ray Diffraction**

Green X-ray quality crystals were obtained by recrystallisation of **2a** and **2c** from DCM/hexane (1:1 v/v) at -20 °C and/or room temperature and from AcOEt/hexane at room temperature for **2b**. X-ray structures and data are presented in Figures 1 and 2 and Tables 1 and 2. As is the case for **2a**,<sup>[3]</sup> the metal ions in **2b** and **2c** display a square-planar geometry (Figures 1 and 2). In all cases, the metal ion is sitting on an inversion centre, and the two five-membered chelate rings are coplanar with no axially coordinated solvent molecule. There are few examples of square-planar coordination geometries reported for cobalt(II) complexes of bidentate ligands,<sup>[3,6a-6c,10,11,12c,14]</sup> since a tetrahedral geometry is favoured on steric grounds in bis(bidentate) four-



Figure 1. ORTEP view of **2b** with  $C_i$  symmetry. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been removed for clarity.



Figure 2. ORTEP view of 2c with  $C_i$  symmetry. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been removed for clarity.

Table 1. Solid-state structure	e and refinement	data for com	pounds 2a-c.
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	<b>2a</b> <sup>[a]</sup>	2b	2c
Formula	C <sub>34</sub> H <sub>38</sub> CoN <sub>4</sub> O <sub>2</sub>	$C_{50}H_{70}CoN_4O_2$	C <sub>38</sub> H <sub>46</sub> CoN <sub>4</sub> O <sub>2</sub>
$M_{w} [\text{gmol}^{-1}]$	593.61	818.03	649.72
Temperature [K]	200	150	150
Wavelength [Å]	0.71073	1.54178	1.54178
Crystal system	monoclinic	triclinic	monoclinic
a [Å]	8.8879(12)	10.6229(3)	7.5524(2)
b [Å]	8.3485(11)	10.6858(2)	24.9130(7)
c [Å]	20.363(3)	11.8393(2)	9.3964(3)
	90	109.052(1)	90
β [°]	93.057(2)	105.705(1)	104.449(1)
γ [°]	90	99.860(1)	90
V [Å <sup>3</sup> ]	1508.8(3)	1172.06(4)	1712.04(9)
Space group	$P2_{1}/c$	$P\overline{1}$	$P2_1/c$
Z	2	1	2
$d_{\text{calcd.}} [\text{g cm}^{-3}]$	1.307	1.159	1.260
$\mu \text{ [mm^{-1}]}$	0.606	3.177	4.223
F(000)	626	441	690
Reflections collected	36660	18441	34923
Independent reflections	4749	18441	3218
GoF	0.975	1.046	1.060
$R_1(\mathbf{F}) \left[ I > 2\sigma(I) \right]$	0.0367	0.0327	0.0298
$wR(F^2)$ $[I > 2\sigma(I)]$	0.1008	0.0829	0.0860
$R_1(F)$ (all data)	0.0512	0.0341	0.0313
$wR(F^2)$ (all data)	0.1066	0.0841	0.0869
Largest difference peak/hole [eÅ <sup>-3</sup> ]	0.858/-0.336	0.153/-0.293	0.272/-0.478

[a] From ref.<sup>[3]</sup>



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Table 2. Selected bond lengths [Å] and an	ingles [°] for 2a–c and chosen	examples of cobalt	complexes from th	ne literature: 3–8.
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Compound	τ4 <sup>[i]</sup>		Bon	Angle [°]	Tilt ang	Tilt angle <sup>[k]</sup> [°]			
-		Co-O1	Co-N2	C1–N1	C1–N2	01-N1	O1–Co–N2	Ar(NO)	ArN
<b>2a</b> <sup>[a]</sup>	0.00	1.834(1)	1.886(1)	1.319(2)	1.312(2)	1.392(1)	84.5(1)	59(1)	79(1)
2b	0.00	1.841(2)	1.883(1)	1.319(2)	1.306(3)	1.389(2)	84.9(1)	84(1)	87(1)
2c	0.00	1.833(1)	1.898(1)	1.316(2)	1.316(2)	1.387(1)	84.6(1)	60(1)	60(1)
<b>3</b> <sup>[b]</sup>	0.00	1.805(3)	1.856(3)			1.339(4)	81.9(1)	_	39(1)
<b>4</b> <sup>[c]</sup>	0.02	1.823(3) <sup>[j]</sup>	1.836(3) <sup>[j]</sup>	_	_	_ ``	85.7(1)	_	90(1)
<b>5</b> <sup>[d]</sup>	0.00	1.828(1)	1.840(1)	_	_	_	85.7(1)	_	69(1)
<b>6</b> <sup>[e]</sup>	0.02	1.848(3) <sup>[j]</sup>	$1.841(4)^{[j]}$	_	_	_	94.1(1)	_	_
<b>7</b> <sup>[f]</sup>	0.00	1.848(1) <sup>[j]</sup>	$1.967(1)^{[j]}$	_	_	_	84.3(1)	_	_
<b>8</b> <sup>[g]</sup>	0.00	1.846(1)	1.938(1)	_	_	_	84.5(1)	_	_
2a-sqpl <sup>[h]</sup>	0.00	1.839	1.890	1.324	1.317	1.398	84.4	74	89
(DFT-optimized CH <sub>2</sub> Cl <sub>2</sub> )									

[a] From ref.<sup>[3]</sup> [b] 3: Co(L)<sub>2</sub>, L = triazene 1-oxide type.<sup>[12c]</sup> [c] 4: Co(L)<sub>2</sub>, L = *o*-aminophenol-type.<sup>[14d]</sup> [d] 5: Co(L)<sub>2</sub>, L = *o*-aminophenol-type.<sup>[14b]</sup> [e] 6: Co(L)<sub>2</sub>, L = [N<sub>2</sub>O<sub>2</sub>] Schiff base type.<sup>[21]</sup> [f] 8: Co(L)<sub>2</sub>, L = *a*-imino alkoxide type.<sup>[11]</sup> [g] 9: Co(L)<sub>2</sub>, L = carbohydrazide-type.<sup>[14e]</sup> [h] Theory level: uB3LYP/LANL2DZ; CPCM: CH<sub>2</sub>Cl<sub>2</sub>. [i] As defined by Houser.<sup>[22]</sup> [j] Average value. [k] Angle between the plane of the aromatic ring and the plane of the –N–C=N– moiety.

coordinate environments. In some cases, axial coordination of solvent molecules is present, which offers the preferred octahedral geometry around the metal centre, as for Co- $(acac)_2$ .<sup>[15]</sup> Stabilization of the square-planar geometry can usually be achieved in the presence of macrocyclic ligands<sup>[16]</sup> or by a special combination of steric and electronic factors.<sup>[3,10,12c,14b,14d]</sup> Square-planar cobalt(II) complexes with bidentate *N*,*O*-ligands that form five-membered chelate rings are rare, and only ten (including **2a**) crystal structures of this type are reported in the CCDC.<sup>[17]</sup>

Five of these structures correspond to cobalt complexes of redox-active *o*-aminophenol-type ligands and can be considered as a special case due to the "noninnocent" nature of the ligand.<sup>[14b,14d,18]</sup> In one other case, the stabilization of the square-planar geometry at the Co centre is assisted by two intramolecular interactions of the X–H···Co type.<sup>[19]</sup> This leaves only three other types of *N*,*O*-ligands, except the AMOXs, able to stabilise the square-planar geometry of cobalt(II) bis(chelates) with five-membered chelate rings:  $\alpha$ -imino alkoxide,<sup>[11]</sup> carbohydrazide<sup>[14e]</sup> and triazene 1-oxide derivatives.<sup>[12c]</sup>

The Co–O bond lengths in 2a-c are similar, and their values are closer to those observed in cobalt complexes of Schiff base type,  $\alpha$ -imino alkoxide type and carbohydrazide-type ligands (compounds 6, 7 and 8; Table 2) rather than the triazene 1-oxide analogues (3; Table 2) or the cobalt(II) complexes of redox-active ligands (4, 5; Table 2). The Co–N bonds are also similar within the 2a-c series, but they differ from those in compounds 3–8 (Table 2) as result of the differences in the five-membered chelate rings (type of atoms, substituents, electronic delocalisation).

All three structures  $2\mathbf{a}-\mathbf{c}$  show electron density delocalised over the amidine bridge, resulting in equal (within  $3\sigma$ ) C1–N1 and C1–N2 bond lengths. However, only partial orbital overlap exists between the aryl and the amidine  $\pi$ -systems, since the aryl rings are twisted from the mean plane of the –N–C=N– moiety in order to accommodate the steric bulk generated by the 2,6-substituents. The values of the tilt angles are shown in Table 2 and are indicative of the degree of delocalisation in the molecule. Among **2a–c**, the largest ArN and Ar(NO) dihedral angles are observed for **2b**. This fact is in accordance with **1b** being the sterically most demanding ligand.

Examination of the packing in the three structures shows weak C( $\pi$ )–H···O (d = 2.45 Å,  $\theta = 162^{\circ}$ ) and C( $\pi$ )–H··· $\pi$ intermolecular interactions for **2a** and **2c**, respectively.

#### <sup>1</sup>H NMR Spectroscopy

The <sup>1</sup>H NMR spectroscopic signals of 2a-c are shifted due to paramagnetic effects (from  $\delta = 69$  ppm to  $\delta =$ -200 ppm; Table 3 and Figure S1, Supporting Information), which is consistent with the oxidation state of the metal ion [cobalt(II), d<sup>7</sup>]. They exhibit characteristically broadened signals, without coupling constants, albeit with accurate integrations. Thus, it was possible to assign the <sup>1</sup>H NMR resonances based on the integration ratio, 2D COSY and T1 relaxation time measurement experiments, and to correlate these results with the proximity of the protons to the metal centre. The aryl ring on the N-Co is closer to the metal centre and thus more influenced than the aryl ring, which sits on the NO-Co.<sup>[20]</sup> As a consequence, the para H4' resonances are paramagnetically more shifted than the para H4 resonances (see Scheme 1 for the notation of H). In the case of **2a** this is also supported by the *T*1 relaxation time values of 22.7 ms for H4 vs. 34.4 ms for H4'. For 2a (substituted with methyl groups in the 2,6-positions), the two broad signals at  $\delta = +37.0$  and -40.1 ppm integrate to 6 H, corresponding to the  $-CH_3$  protons. They are positioned in close proximity to the cobalt centre due to the tilt of the aryl rings with respect to the amidine oxide plane. Their short T1 relaxation time values of 1.3 and 1.7 ms are also in line with their position close to the paramagnetic centre. In the case of **2b**, the  $-CH-CH_3$  protons are the ones close to the metal centre, and their resonances are thus the most shifted due to paramagnetism, being observed as broad signals at  $\delta$  = +18.1 and -26.9 ppm. Their resonances are observed as



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Table 3. Chemical shift values (ppm) for <sup>1</sup>H NMR spectra<sup>[a]</sup> of complexes 2a-c.<sup>[b]</sup>

Compound	1	3'	3	4′	4	5′	5	6'	6	$-CH'-CH_3$	-CH-CH <sub>3</sub>	-CH3'	$-CH_3$
2a	-0.7	-1.6	30.8	-34.3	19.6	-1.6	30.8	_	_	_	_	-40.1	37.0
2b	0.5	8.8	14.8	- 3.7	11.5	8.8	14.8	_	-	-26.9	18.1	-2.5, -16.5	8.0, 0.5
2c	0.1	-9.5	30.3	-34.1	20.1	11.6	33.3	-200	69.2	-22.7	51.1	-29.0	8.9

[a] See Scheme 1 for the notation of the H atoms. [b] In CD<sub>2</sub>Cl<sub>2</sub>.

broad signals at  $\delta = +18.1$  and -26.9 ppm. For compound **2c** (monosubstituted in position 2), protons H6, H6' (in the *ortho* position) and H4' (in the *para* position) are the most influenced by the metal centre, and thus their signals appear at  $\delta = 69.2$ , -200 and -34.1 ppm, respectively.

#### Square-Planar (LS) to Tetrahedral (HS) Isomerisation

In four-coordinate cobalt(II) systems, the square-planar to tetrahedral structural change is also accompanied by a change in spin.<sup>[4]</sup> The solution and solid-state effective magnetic moments for 2a-c are shown in Table 4. The solidstate magnetic moments have the characteristic low spin (LS, S = 1/2) values (1.8–2.2  $\mu_B$ ) expected for cobalt(II) in square-planar geometry.<sup>[4,7]</sup> These values are in line with the square-planar geometry of the compounds as shown by XRD structural characterisation. For 2a, the solutionphase (CH<sub>2</sub>Cl<sub>2</sub>) magnetic moment (4.7  $\mu_B$ ) corresponds to a tetrahedral configuration of the cobalt(II) d<sup>7</sup> centre: highspin, S = 3/2. This value is higher than the spin-only one  $(3.89 \,\mu_B)$  due to spin-orbit coupling.<sup>[23]</sup> The values of the magnetic moment determined in solution for **2b**  $(3.5 \mu_{\rm B})$ and 2c (4.0  $\mu_B$ ) are between the accepted high-spin (4.2– 5.2  $\mu_{\rm B}$ ) and low-spin (1.8–2.2  $\mu_{\rm B}$ ) values<sup>[4]</sup> for cobalt(II) complexes, suggesting an equilibrium between the LS square-planar and HS tetrahedral forms.<sup>[6a,6c,8,20a]</sup>

Table 4. Effective magnetic moments  $\mu_{eff}$   $[\mu_B]$  for complexes  $2a{-}c,$  measured in solution^{[a]} and the solid^{[b]} state.

Compound	$\mu_{\rm eff} \ ({ m solution})^{[c]} \ [\mu_{ m B}]$	$\mu_{\rm eff} \ ({\rm solid \ state})^{[c]} \ [\mu_{\rm B}]$
2a	$4.67\pm0.16$	$1.84\pm0.21$
2b	$3.54 \pm 0.14$	$1.86 \pm 0.16$
2c	$4.03\pm0.06$	$2.10\pm0.09$

[a] Measured by Evans' method in  $CD_2Cl_2$  (10vol.-% TMS) at 298 K. [b] Measured by using a magnetic susceptibility balance at 295 K. [c] The measurements were done at least in triplicate, and the reported error represents the confidence interval at 95% probability.

The thermodynamic parameters for this equilibrium for **2a–c** are presented in Table 5. They were derived based on variable-temperature (193–298 K) magnetic susceptibility measurements. This method was previously reported for similar systems.<sup>[6a,6c,8,24]</sup> The magnetic moment increased with increasing temperature for **2a–c**, with the highest variation in the 193–298 K temperature range being observed for **2b**, followed by **2c** and **2a** (Figure S3, Supporting Information). By using:

Table 5. Thermodynamic parameters related to the isomerisation equilibrium: tetrahedral high-spin (HS) to square-planar low spin (LS) for 2a-c in noncoordinating solvents.<sup>[a]</sup>

Compound	$\Delta G^{298}$ [kJ mol <sup>-1</sup> ]	$\Delta H$ [kJ mol <sup>-1</sup> ]	$\frac{\Delta S}{[\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1}]}$	$N_{\rm t}^{\rm [b]}$
2a	$-5 \pm 0.8$	$5\pm0.9$	$34 \pm 6.1$	$0.9 \pm 0.16$
2b	$1\pm0.2$	$11 \pm 2.0$	$32 \pm 5.8$	$0.4\pm0.07$
2c	$-1 \pm 0.2$	$5\pm0.9$	$18 \pm 3.2$	$0.6\pm0.11$
$Co(RN_3Ar)_2^{[c]}$	_	1-15	5-30	_
$\operatorname{Co}(L)_2^{[d]}$	-	0-12	6–32	-

[a] Derived from magnetic susceptibility measurements performed by Evans' method in CD<sub>2</sub>Cl<sub>2</sub>, at variable temperatures (193– 298 K); corrections for the change in solvent density with temperature were applied,<sup>[25,26]</sup> errors are estimated as follows:  $\pm 4\%$  for the magnetic moments;  $\pm 15\%$  for  $\Delta G$  values (considering an error of 10% on the magnetic moment assumed for the pure tetrahedral form);  $\pm 18\%$  for  $\Delta H$ ,  $\Delta S$  and  $N_t$  values.<sup>[27]</sup> [b]  $N_t$ : mole fraction of the tetrahedral form at 298 K. [c] Cobalt(II) complexes of triazene 1-oxide type ligands.<sup>[14a]</sup> [d] L is a  $\beta$ -ketoamine- or  $\beta$ -iminoaminetype ligand.<sup>[5a]</sup>

$$\mu_{\rm eff} = 2.83 (\chi^M{}_T)^{1/2} \tag{1}$$

the free energy changes ( $\Delta G$ ) were evaluated from the temperature dependence of the magnetic susceptibility ( $\chi^M$ : molar magnetic susceptibility) and hence the corresponding effective magnetic moments:

$$\Delta G = RT \ln \frac{\chi_{\rm t}^{\rm M} - \chi_{\rm obs}^{\rm M}}{\chi_{\rm obs}^{\rm M} - \chi_{\rm p}^{\rm M}} = RT \ln \frac{\mu_{\rm t}^2 - \mu_{\rm obs}^2}{\mu_{\rm obs}^2 - \mu_{\rm p}^2} \tag{2}$$

Expression 2 was derived using Equations (3)–(7):

$$\Delta G = -RT \ln K \tag{3}$$

$$\chi^{M}_{obs} = N_{t}\chi^{M}_{t} + N_{p}\chi^{M}_{p}$$
<sup>(4)</sup>

$$K = \frac{N_{\rm t}}{N_{\rm p}} \tag{5}$$

$$N_{\rm t} + N_{\rm p} = 1 \tag{6}$$

$$N_{\rm t} = (1 + e^{\Delta G/RT})^{-1} \tag{7}$$

The equilibrium constant (*K*) of the square-planar to tetrahedral isomerisation process is defined as in (5), with  $N_t$ and  $N_p$  representing the mole fractions of the tetrahedral and square-planar forms, respectively. The magnetic moments determined for **2a–c** in the solid form (100% squareplanar) were used as magnetic moments of the pure squareplanar form ( $\mu_p$ ). For the pure tetrahedral form ( $\mu_t$ ), magnetic moments of 4.85  $\mu_B$  were assumed, based on literature reports of similar systems.<sup>[4,8]</sup>

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The  $\Delta G$  values for **2a–c** varied linearly with the temperature (Figure S2, Supporting Information). By using:

$$\Delta G = \Delta H - T \Delta S \tag{8}$$

the changes in enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) were obtained from the least-square fit of  $\Delta G$  vs. *T* (Table 5, Figure S2, Supporting Information).

The values of the thermodynamic parameters obtained for the bis(AMOX) cobalt chelates are in the same order of magnitude as those previously reported for cobalt complexes of triazene 1-oxide type<sup>[8]</sup> and β-ketoamine-type<sup>[5a]</sup> ligands. For **2a** and **2c**, the values of  $N_t$  at 298 K (0.9 and 0.6) indicate a preference for tetrahedral geometry in  $CH_2Cl_2$  solution. Interestingly, in the case of **2b**, the squareplanar form is slightly stabilised ( $N_t = 0.4$ ). Thus, the thermodynamic data suggest a high sensitivity of the isomerisation equilibrium to the substitution pattern on the ligand. The higher proportion of the square-planar form (LS) in 2b vs. 2a and 2c also correlates with the UV/Vis spectroscopic data (vide infra) and the chemical shifts in <sup>1</sup>H NMR spectrum, which are the paramagnetically least shifted in the case of 2b. The preference of 2a for the tetrahedral form is also supported by DFT calculations (vide infra). To eliminate the possibility of five- or six-coordinate low-spin species, and hence their influence on the observed magnetic moments, the adherence to the Beer-Lambert law was confirmed in the range of concentrations over which the magnetic and spectroscopic properties were measured  $(10^{-5}-10^{-3} \text{ M})$ .<sup>[6b]</sup> This would not be the case if dimerisation promoted octahedral coordination at higher concentrations.

As for the other cases of square-planar to tetrahedral isomerisation, positive values are obtained for  $\Delta H$ , which can be attributed to the endothermic weakening of the metal-ligand bonds in the isomerisation process.<sup>[5a,8]</sup> The highest value of  $\Delta H$  is observed for **2b**, indicating a higher degree of stabilisation for the square-planar form in this case. The high steric bulk of the 2,6-di-*i*Pr substituents on the aryl rings pushes the phenyl rings almost perpendicular to the plane of the amidine backbone (tilt angles of 84° and 87°; see Table 2). Therefore, the electronic density of the anionic -O-N-C=N-AMOX linkage is less delocalised on the aromatic moieties of the ligand thereby generating a stronger ligand field for the metal centre.

The total entropy change  $\Delta S$  is considered to have three contributions: the change in spin multiplicity, the difference in solvation and the change in vibrational entropy between the two isomers.<sup>[16]</sup> While the change in spin multiplicity

(doublet to quartet) is the same for all three compounds, it is difficult to distinguish between the specific contributions in terms of solvation and vibrational entropy due to the bulky substituents on the aryl rings. Complexes **2a** and **2b** are *ortho*-disubstituted on the aryl rings and present similar values for the entropy change vs. *ortho*-monosubstituted **2c**, for which a decrease in  $\Delta S$  can be observed.

## **UV/Vis Spectroscopic Properties**

The spectroscopic properties of 2a-c are presented in Table 6. Their UV/Vis spectra in CH<sub>2</sub>Cl<sub>2</sub> show low-intensity bands in the visible and NIR region, with intense bands centred at higher energies than the solvent cut-off point (Figure 3 and Figure S4, Supporting Information). The absorption bands in the visible and NIR region correspond to spin-allowed and Laporte-forbidden dd transitions. They present characteristic low molar absorptivity values.<sup>[23,28]</sup> The bands at 540-550 nm, 940-980 nm and 1230 nm are characteristic of the tetrahedral form.<sup>[5a,8]</sup> Similar features were identified for tetrahedral cobalt(II) complexes of triazene 1-oxides<sup>[8]</sup> and  $\beta$ -ketoamine<sup>[5a]</sup> ligands. These three transitions could be tentatively assigned, based on Orgel diagrams for tetrahedral metal complexes, to  ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(P)$ ,  ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{1}(F)$  and  ${}^{4}A_{2}(F) \rightarrow {}^{4}T_{2}(F)$ , respectively.<sup>[23,28]</sup> The analysis of the electronic spectra of 2a and 2c shows that UV/Vis spectroscopy also supports the existence of tetrahedral geometry in solutions of noncoordinating solvents for these complexes at room temperature.



Figure 3. Electronic spectra of 2a-c in  $CH_2Cl_2$  at room temperature.

Table 6. Spectroscopic data for complexes 2a-c and their corresponding ligands 1a-c.<sup>[a]</sup>

1	
Compound	$\lambda_{\max} \text{ [nm]} (\varepsilon  imes 10^2 \text{ [m}^{-1} \text{ cm}^{-1} \text{]})$
1a	286 (130)
1b	280 (110)
1c	293sh (120), 313 (154)
2a	247sh (239), 265sh (209), 350 (32), 540 (0.97), 622 (0.32), 942 (0.29), 1233 (0.27)
2b	260sh (253), 340 (55), 550 (0.40), 635 (0.24), 945 (0.15), 1000sh (0.11), sh1310 (0.11)
2c	290 (196), 305 (176), 540 (0.57), 644sh (0.18), 987 (0.16), 1247 (0.20)

[a] Measured in dichloromethane, at room temperature; sh = shoulder.

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Figure 4 presents the comparison of the electronic spectra of **2a** recorded in  $CH_2Cl_2$  at 298 K and 188 K. The band at 620–640 nm is indicative of the square-planar form. A second band characteristic of the square-planar isomer appears at 900–1000 nm, but overlaps with the signal identified for the tetrahedral form.<sup>[6c,8]</sup> The square-planar form is stabilised with decreasing temperature.



Figure 4. Electronic spectra of 2a in  $CH_2Cl_2$  at 298 K (red) and 188 K (black).

The absorption spectrum of **2b** confirms that the squareplanar form is present in a higher proportion compared with **2a** and **2c** at room temperature. The variable-temperature UV/Vis analysis for **2b** further indicates an increase in the square-planar form with decreasing temperature (Figure 5). Its comparison with the absorption spectrum of **2b** in the solid state (Figure 6) confirms the assignment of the band at 620–640 nm to the square-planar form.



Figure 5. Electronic spectra of  $\mathbf{2b}$  in  $\mathrm{CH}_2\mathrm{Cl}_2$  at variable temperature.

For the AMOX ligands **1a–c** the electronic spectra display the characteristic ligand-centred (LC)  $\pi$ – $\pi$ \* transitions in the UV region, with high molar absorptivity coefficients (Figure S4, Supporting Information).<sup>[23,28]</sup>

## **DFT Calculations**

The optimised structures of 2a for the two forms [squareplanar (S = 1/2, doublet) (2a-sqpl) and tetra-



Figure 6. Electronic spectra of 2b in  $CH_2Cl_2$  at 298 K (red), 188 K (black) and in the solid state (green).

3/2, quadruplet) (2a-tetra)] in dihedral (S = chloromethane (spin-unrestricted uB3LYP/LANL2DZ theory level; CPCM: CH<sub>2</sub>Cl<sub>2</sub>) are illustrated in Figure 7a. The optimised calculated structure of 2a-sqpl is in good agreement with the XRD data (Table 2). The comparison of the energy values of the two isomers 2a-sqpl and 2a-tetra (Table S1, Supporting Information) shows a slight stabilisation (4.3 kcalmol<sup>-1</sup>) of the tetrahedral form, which is in accordance with the experimental observations and the values of the thermodynamic parameters. In an effort to account for the preference for the square-planar form in the case of **2b**, DFT calculations using the same theory level were also run for its two isomers **2b**-sqpl (S = 1/2, multiplicity doublet) and **2b**-tetra (S = 3/2, multiplicity quadruplet) (Tables S1-S3, S6, S7, Supporting Information). Nonconvergence of the 2b-sqpl frequency calculation does not allow us to conclude if this structure is at its minimum and, therefore, the energy comparison is inconclusive in this case.



Figure 7. (a) DFT-optimised structures (uB3LYP/LANL2DZ; CPCM: CH<sub>2</sub>Cl<sub>2</sub>) for the square-planar (S = 1/2, doublet) and the tetrahedral (S = 3/2, quadruplet) form of **2a**; (b) electron-spin density plots for the two isomers of **2a**.

Figure 7b displays the spin-density plots for each of the two isomers of **2a**. The corresponding values are illustrated in Table S2, Supporting Information. The unpaired elec-

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trons are concentrated on the metal centre ( $d_{yz}$  orbital for the square-planar form;  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbitals for the tetrahedral form). The same observation stands for **2b**.

#### Electrochemistry

Table 7 presents the electrochemical data for 2a-c in DCM and DMF. The CVs. (Figure S5, Supporting Information) display a one-electron reversible process, assigned to the Co<sup>II/III</sup> couple, followed by irreversible ligand-based oxidation processes. The easier oxidation of 2a-c in DMF (0.09–0.17 V) than in DCM (0.41–0.47 V) can be seen as a consequence of the difference in coordination capacity and polarity of the two solvents. It is worth mentioning that no reduction wave can be observed for 2a-c in the electrochemical window of DCM (down to -1.8 V). The same observation was reported for the cobalt(II) complexes of triazene 1-oxides.<sup>[8]</sup> The difficult reduction is in line with the anionic character of the ligand, enhanced by the effect of the electron-donating substituents. However, an irreversible reduction process can be observed in DMF, in the -2.16 to -2.34 V potential range. This process is absent in the CV of the free ligand (Figure S5, Supporting Information), and it is therefore tentatively assigned to the Co<sup>II/I</sup> reduction.

Table 7. Electrochemical data for compounds  $2a{-}c$  in dry DCM and DMF.  $^{[a,b]}$ 

Compound			<i>E</i> [V	] vs. SCE		
	$E_1$	2 <sup>[c]</sup>	I	E <sub>pa</sub> (irr)	$E_{\rm pc}(\rm irr)$	
	DCM	DMF	DCM	DMF	DCM	DMF
2a	0.47	0.14	1.70 <sup>[d]</sup>	1.06, 1.22,	_[e]	-2.27
	(70)	(62)		1.57		
2b	0.41	0.17	1.88	1.15, 1.38,	_[e]	-2.34
	(80)	(76)		1.56		
2c	0.46	0.09	1.56	0.92, 1.21	_[e]	-2.16
	(82)	(86)				

[a]  $[nBu_4N]PF_6$  (0.1 M), compound concentration about 1 mM, glassy carbon electrode, scan rate 100 mV/s, room temperature, Ar, ferrocene used as internal reference. [b] All potentials are reported in V, vs. SCE (Fc/Fc<sup>+</sup> vs. SCE was considered 0.46 V in DCM and 0.45 V in DMF.<sup>[29]</sup>). [c] The difference  $E_{pc} - E_{pa}$  is given in parentheses. [d] From ref.<sup>[3]</sup> [e] No process is observed.

## Conclusions

New bis(AMOX) cobalt(II) complexes were synthesised and characterised. They are a new family of compounds that isomerise from square-planar LS in the solid state to tetrahedral HS in solutions of noncoordinating solvents. This process was probed by the crystal structures of the compounds showing square-planar geometry at the metal centre, and the magnetic moments in the solid state with values characteristic of the LS form. NMR spectroscopic data, values of solution magnetic moments and UV/Vis data are in agreement with the existence of an equilibrium between the square-planar and tetrahedral forms in solutions of noncoordinating solvents. The thermodynamic parameters for the isomerisation equilibrium were determined. They suggest a major influence of the ligand substitution pattern on the isomerisation equilibrium by a subtle interplay of steric and electronic factors. Very bulky substituents in 2,6-positions of the aryl rings of the ligand favour the square-planar (LS) form in the solid state, and in solutions of noncoordinating solvents. An extended delocalisation of the electron density of the amidine N-oxide moiety is hindered in this case by steric factors (tilt angles formed by the aryl planes and the five-membered chelate ring plane are close to 90°). As observed, slightly less bulky substituents (2-iPrPh and 2,6-Me<sub>2</sub>Ph) still stabilise the squareplanar form in the solid state. In solutions of noncoordinating solvents at room temperature, however, they allow tilt angles more favourable to an enhanced delocalisation of the electron density of the amidine N-oxide moiety, reducing the field strength of the corresponding ligands and stabilising the tetrahedral form. This is also confirmed by DFT calculations, in the case of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub> substituents. The fact that the square-planar form stabilises with decreasing solution temperature is in line with the explanations given above.

The extra substitution position available on the central C atom in the AMOX ligand system can be seen as an advantage in terms of steric modularity and electronic tuning (e.g. compared with the triazene 1-oxide analogues). We are extending the family of AMOX-based metal complexes in order to better assess and understand the interplay of steric and electronic factors and their influence on the properties in these systems.

# **Experimental Section**

Materials and Instrumentation: The metal salts, anilines and triethyl orthoformate were purchased from Aldrich, and *m*-CPBA (77%) was purchased from Acros. All were used without further purification. ACS grade solvents were purchased from VRW and Fisher and were removed under reduced pressure using a rotary evaporator, unless otherwise stated. Nuclear magnetic resonance (NMR) spectra were recorded in CD<sub>2</sub>Cl<sub>2</sub> and CDCl<sub>3</sub> at 25 °C, with the following spectrometers: Bruker AV-400, AV-500 and DRX-400. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to TMS, and are referenced to the residual solvent signal ( $\delta$  = 5.35 ppm for CD<sub>2</sub>Cl<sub>2</sub> and 7.26 ppm for CDCl<sub>3</sub>). Variable-temperature NMR spectra and T1 relaxation-time measurements were performed at the NMR Spectroscopy Service of the Université de Montréal. Absorption spectra were measured in dichloromethane (previously distilled), between 230 and 1400 nm, at room temperature (room temp.), with a Cary 500i UV/Vis/NIR spectrophotometer. Absorption spectra at variable temperature were measured with a Cary 6000i UV/Vis/NIR spectrophotometer by using an Oxford Instrument cryostat and temperature controller. Solution samples were prepared in the concentration range of  $10^{-5}$  to  $10^{-3}$  M. The absorption spectrum of 2b in the solid state was measured with the latter instrument, by using a microcrystal mounted on a solid sample holder. Electrochemical measurements were carried out in argon-purged dry DCM, at room temperature, with a BAS CV50W multipurpose instrument interfaced with a PC. The working electrode was a glassy carbon electrode. The counter electrode was a Pt wire, and the pseudo-reference electrode was a silver wire. The reference was set using an internal 1 mM ferrocene/ferrocenium

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sample at 460 mV and 450 mV vs. SCE in DCM and DMF, respectively.<sup>[29]</sup> The concentration of the compounds was about 1 mM. Tetrabutylammonium hexafluorophosphate (TBAP) was used as the supporting electrolyte, and its concentration was 0.10 M. Cyclic voltammograms were obtained at scan rates of 50, 100, 200 and 500 mVs<sup>-1</sup>. For irreversible oxidation processes, the anodic peak was used as E. Experimental uncertainties are as follows: absorption maxima,  $\pm 2$  nm; molar absorption coefficient, 10%; redox potentials,  $\pm 10$  mV. The microanalyses and the mass spectrometry analyses were performed at the Elemental Analysis Service and the Regional Mass Spectrometry Centre of the Université de Montréal. Magnetic susceptibility measurements in solution were performed by Evans' method,<sup>[24]</sup> in CD<sub>2</sub>Cl<sub>2</sub>, by using 10% vol.-% TMS at 298 K. The sample concentration was in the order of  $10^{-3}$  M. In the solid state, the measurements were carried out on powder or microcrystalline samples (10-20 mg), at 295 K, by using a Johnson-Matthey magnetic susceptibility balance and HgCo(NCS)<sub>4</sub> as calibrant.<sup>[30]</sup> The measurements were performed at least in triplicate, and the confidence interval at 95% probability is given as the error. The standard diamagnetic corrections using Pascal's constants were applied.<sup>[31]</sup> Magnetic moments were calculated by using:

$$\mu_{\rm eff} = 2.83 (\chi^M{}_T)^{1/2} \tag{9}$$

As previously reported<sup>[6a,6c,8,24]</sup> and succinctly presented in the Results and Discussion section, magnetic susceptibility measurements in solution (Evans' method) were performed at variable temperature (193–298 K) in order to derive thermodynamic parameters for the isomerisation equilibrium discussed in this paper.

X-ray Structure Determination: Crystal structure determination and refinement data for 2a–c are given in Tables 1 and 2 and Figures 1 and 2. Details are provided in the Supporting Information. CCDC-963737 (for 2b) and -963738 (for 2c) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

Computational Details: Gaussian 09, Revision D.01<sup>[32]</sup> was used for all theoretical calculations discussed herein, with the spin-unrestricted B3LYP<sup>[33]</sup> DFT method, LANL2DZ ECP<sup>[34]</sup> basis set and CPCM (CH<sub>2</sub>Cl<sub>2</sub>) solvation model. Initial atom coordinates for geometry optimisation were taken from XRD data (cif) of the corresponding square-planar structures. For the tetrahedral isomers, XDR data of the Zn analogues (of tetrahedral geometry) were used, with the Zn atom changed for a Co atom. No symmetry constraints were used for the geometry optimisation. Details of optimised structures are given in Tables S4-S7, Supporting Information. No imaginary frequencies were obtained when frequency calculations on optimised geometries were performed, except for 2b-sqpl (see DFT calculations part in this paper and the Supporting Information). The values of  $\langle S^2 \rangle$  were monitored and did not show major spin contamination (Table S3, Supporting Information). The total energy values used for calculating energy differences between isomers were obtained from single-point calculations on the optimised structures using a mixed basis set: LANL2DZ ECP for the Co atom and 6-311g(d,p) for the N, O, C and H atoms. GaussView 3.0.9<sup>[35]</sup> and Chemissian 2.200<sup>[36]</sup> software were used for data analysis, visualisation and surface plots.

Synthesis: The syntheses of ligands 1a-c and complex 2a were previously reported.<sup>[3,13]</sup>

## Synthesis of Complexes

**General Procedure:**  $^{[1c,3]}$  A solution of the ligand (2 equiv.) in aqueous ethanol (90 vol.-%) was added to a solution of metal salt

(1 equiv.) in water. The formation of a precipitate was observed almost instantly. The reaction mixture was stirred at room temperature before water was added (reaction times are specified below for each compound) and was kept at 4 °C for 1–2 h before being filtered. The resultant solid was washed with hot water and aqueous ethanol (50 vol.-%) and was taken up in DCM and dried with MgSO<sub>4</sub>. A second filtration and solvent evaporation yielded the desired products as solids. When necessary, further purification by recrystallisation was performed.

Bis[N,N'-bis(2,6-diisopropylphenyl)-N-oxidoformamidinate] of Cobalt(II) (2b): The following reagents were combined according to the general procedure: N-hydroxy-N,N'-bis(2,6-diisopropylphenyl)formamidine (1b) (0.40 g, 1.1 mmol, 2 equiv.) and cobalt(II) acetate tetrahydrate (0.13 g, 0.51 mmol, 1 equiv.). Reaction time: 90 min. Yield 0.33 g, 83%. Green crystals (X-ray quality) were obtained after recrystallisation in AcOEt/hexane (1:1). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 18.13$  (s, 2 H, -CH-CH<sub>3</sub>), 14.79 (s, 2 H, -m-C<sub>6</sub>H<sub>3</sub>), 11.49 (s, 1 H, -p-C<sub>6</sub>H<sub>3</sub>), 8.83 (s, 2 H, -m-C<sub>6</sub>H<sub>3</sub>), 8.00 (s, 6 H, -CH-CH<sub>3</sub>), 0.54 (s, 7 H, -CH-CH<sub>3</sub> and -N-CH=N-), -2.50 (s, 6 H, -CH-CH<sub>3</sub>), -3.71 (s, 1 H, -p-C<sub>6</sub>H<sub>3</sub>), -16.45 (s, 6 H, -CH-CH<sub>3</sub>), -29.91 (s, 2 H, -CH-CH<sub>3</sub>) ppm. C<sub>50</sub>H<sub>70</sub>CoN<sub>4</sub>O<sub>2</sub> (818.06): calcd. C 73.41, H 8.62, N 6.85; found C 73.41, H 8.90, N 6.87. MS (ESI, DCM):  $m/z = 817.4 \text{ [M]}^+$ . IR (ATR, solid sample):  $\tilde{v} = 3066, 3028, 2959,$ 2927, 2864, 1608, 1586, 1461, 1442, 1404, 1380, 1360, 1327, 1306, 1270, 1254, 1214, 1191, 1178, 1099, 1060, 1043, 992, 930, 886, 820, 801, 770, 756, 731, 689, 642, 620, 599, 546, 534, 497, 485, 427 cm<sup>-1</sup>.

Bis[*N*,*N*′-bis(2-isopropylphenyl)-*N*-oxidoformamidinate] of Cobalt(II) (2c): The following reagents were combined according to the general procedure: N-hydroxy-N,N'-bis(2-isopropylphenyl)formamidine (1c) (0.29 g, 1.0 mmol, 2 equiv.) and cobalt(II) acetate tetrahydrate (0.13 g, 0.51 mmol, 1 equiv.). Reaction time: 90 min. Product obtained as green powder. Yield 0.29 g, 87%. Recrystallisation in DCM/hexane (1:1) at room temperature afforded X-ray quality green crystals. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  = 69.21 (s, 1 H, -o-C<sub>6</sub>H<sub>4</sub>), 51.14 (s, 1 H, -CH-CH<sub>3</sub>), 33.29 (s, 1 H, -m-C<sub>6</sub>H<sub>4</sub>), 30.32 (s, 1 H, -m-C<sub>6</sub>H<sub>4</sub>), 20.10 (s, 1 H, -p-C<sub>6</sub>H<sub>4</sub>), 11.66 (s, 1 H, -m-C<sub>6</sub>H<sub>4</sub>), 8.87 (s, 6 H, -CH-CH<sub>3</sub>), 0.12 (s, 1 H, -N-CH=N-), -9.54 (s, 1 H, -m-C<sub>6</sub>H<sub>4</sub>), -28.99 (s, 6 H, -CH-CH<sub>3</sub>), -32.67 (s, 1 H, -CH-CH<sub>3</sub>), -34.12 (s, 1 H, -p-C<sub>6</sub>H<sub>4</sub>), -200.6 (s, 1 H, -o-C<sub>6</sub>H<sub>4</sub>) ppm. C<sub>38</sub>H<sub>46</sub>CoN<sub>4</sub>O<sub>2</sub> (649.74): calcd. C 70.25, H 7.14, N 8.62; found C 70.43, H 7.13, N 8.60. MS (ESI, DCM):  $m/z = 650.2 \text{ [M + H]}^+$ . IR (ATR, solid sample):  $\tilde{v} = 3066, 3027, 2955, 2927, 2859, 1605,$ 1586, 1572, 1495, 1484, 1446, 1407, 1379, 1360, 1295, 1276, 1243, 1227, 1198, 1162, 1113, 1093, 1085, 1035, 997, 938, 888, 863, 823, 775, 755, 679, 638, 628, 538, 507, 468, 436 cm<sup>-1</sup>.

## Acknowledgments

We are grateful to the Natural Sciences and Engineering Research Council (NSERC) of Canada, the Fonds québécois de la recherche sur la nature et les technologies (FQRNT), the Centre for Self Assembled Chemical Structures (CSACS), and the Université de Montréal for financial support. M. C. thanks NSERC for a Canada Graduate Scholarship and FQRNT for a Doctoral Scholarship (A7). The authors thank Alexandre Rodrigue-Witchel, PhD, Andréanne Bolduc, PhD, Nicolas Bélanger Desmarais, and Professor Christian Reber for their assistance with the absorption measurements. M. C. thanks Daniel Chartrand and Amlan Pal for useful scientific discussions. The authors are also grateful to Compute Canada and to UdeM NMR, EA, XRD, and MS services and personnel for their help.

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Received: September 21, 2014 Published Online: ■

Pages: 11

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# Amidinate N-Oxide Complexes

M. Cibian, S. Langis-Barsetti, F. G. De Mendonça, S. Touaibia, S. Derossi, D. Spasyuk, G. S. Hanan<sup>\*</sup> ...... 1–11

Influence of Ligand Substitution Pattern on Structure in Cobalt(II) Complexes of Bulky N,N'-Diarylformamidinate N-Oxides

**Keywords:** Cobalt / N,O ligands / Substituent effects / Structure elucidation / Stereochemistry



Cobalt(II) bis(chelates) of bulky *N*,*N*'-diarylformamidinate *N*-oxide ligands show isomerization from square-planar low-spin (in the solid state) to tetrahedral high-spin (in solutions of noncoordinating solvents).