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Synthesis and Structural Studies of Two New Base Adducts of Bis(2,4-pentanedionato)cobalt(II)

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Keywords: Cobalt / 2,4-Pentanedione / 3,5-Dimethylpyrazole / Dimethylethanolamine / Coordination modes

The syntheses, spectroscopic properties and crystal structures of two new base adducts of bis(2,4-pentanedionato)cobalt(II) with 3,5-dimethylpyrazole (Hdmpz) (**1**) and dimethylethanolamine (Hdmea) (**2**) are described. The crystal structures of both compounds contain monomeric Co^{II} complexes with *cis*-distorted octahedral environments, even for the monodentate Hdmpz ligand which is quite unique. These mononuclear complexes are linked by hydrogen bonds between the anionic 2,4-pentanedionato groups and the neutral Hdmpz or Hdmea ligands. The low-temperature polycrystal-

line-powder EPR spectra display unresolved metal hyperfine coupling. The *g* values are anisotropic in both cases; the anisotropy is larger for the Hdmea adduct. Interesting insights into the coordination effects were gained with the help of electron-density descriptors (Laplacian of density and Natural Bond Orbitals). This revealed a slight deviation of the coordinating lone pairs of the pentanedionato ligands from the Co–O axis, as well as a nonstandard hybrid composition. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

The β -diketonato complexes of cobalt(II) are of interest in the field of coordination chemistry as structural prototypes and because of their tendency to form unanticipated oligomeric structures where the metal centre achieves a coordination number greater than four. Bis(acetylacetonato)cobalt(II) is a very common and easily accessible coordination complex, which exists as a tetranuclear complex in nonpolar solvents.^[1] If a small amount of some neutral donor ligand (L) is introduced into a solution of the tetrameric Co(acac)₂ in a noncoordinating solvent, complex equilibria involving the following types of compounds are established: [Co(acac)₂]₄, [Co(acac)₂L], [Co(acac)₂L]₂ and [Co(acac)₂L₂].^[2] Thus, upon treatment of [Co(acac)₂]₄ with pyridine (py), the compound *trans*-[Co(acac)₂py₂] was isolated and its structure determined.^[3] Similarly, *trans*-[Co(acac)₂L₂] compounds (where L represents water, 6-methyl-

quinoline, imidazole and 2-aminopyridine) were also prepared and their crystal structures reported.^[4–7] With water as the donor molecule, two intermediate products were isolated: [Co(acac)₂(H₂O)]₂ and [Co(acac)₂]₃(H₂O).^[8,9] The crystal structures of both are derived from that of the tetrameric complex [Co(acac)₂]₄.

Our current interest in the autoxidation drying mechanism occurring in alkyd paints,^[10,11] which involves cobalt complexes that are present as additives, led us to investigate the coordination chemistry and the catalytic activity of bis(2,4-pentanedionato)cobalt(II) in the presence of some organic ligands as possible co-catalysts.^[12] In this context, it is of interest to probe the stability and reactivity of such adducts and additional information can be gained by contrasting the properties of chelating ligands, constrained to adopt *cis* geometry, with those of monodentate ligands, which typically yield *trans* complexes.^[13]

In this paper, the syntheses, crystal structures and spectroscopic properties of *cis*-[Co(acac)₂(Hdmpz)₂] (**1**) and [Co(acac)₂(Hdmea)] (**2**) are described. Both complexes are new base adducts of bis(2,4-pentanedionato)cobalt(II) with Hdmpz (3,5-dimethylpyrazole) or Hdmea (dimethylethanolamine). Furthermore, compound **1** offers an interesting chromophore, distinguished as having the anisotropy of π effects in the N–Co–N moiety qualitatively different (in-plane) as compared to those encountered in chelating diamines (perpendicular to the N–Co–N plane).

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Results and Discussion

Synthetic and Spectroscopic Studies

The compounds *cis*-[Co(acac)₂(Hdmpz)₂] (**1**) and [Co(acac)₂(Hdmea)] (**2**) were obtained in good yields by adding a stoichiometric amount of either Hdmpz or Hdmea to a solution of anhydrous cobalt acetylacetonate in toluene. Suitable crystals were obtained by slow evaporation of the solvent. Although compound **1** appeared to be unstable in solution (see below), the reaction that forms the oxidized product is sufficiently slow to allow the crystallisation of the pure cobalt(II) complex. The IR spectra of both compounds show the bands expected for the organic ligands coordinated to the cobalt centre. In particular, the peak at $\tilde{\nu} = 3348\text{ cm}^{-1}$ observed in the IR spectrum of **2**, indicates the presence of the protonated ligand Hdmea.

The solid-state electronic spectra of both compounds show two principal regions of absorption, as expected for octahedral Co^{II} complexes. The absorption spectrum of compound **1** is dominated by a broad band with a maximum at 1170 nm and a multicomponent band at 510 nm which together suggest the presence of pseudo-octahedral high spin Co^{II} centres. Compound **2** has a similar absorption spectrum with two main bands, one at 1125 nm and the other at 502 nm. These two bands correspond to the $^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$ transitions. The multiple structure of the band near 500 nm arises from a number of effects, but primarily from the admixture of spin-forbidden transitions to doublet states mainly derived from 2G and 2H .^[14]

Study of the complexation reaction that occurs upon adding Hdmpz or Hdmea to [Co(acac)₂(H₂O)₂] in various solvents (methanol, ethanol, acetone, benzene and toluene) reveals that compounds with the composition [Co(acac)₂(Hdmpz)₂] or [Co(acac)₂(Hdmea)] are formed, irrespective of the nature of the solvent used. The electronic spectrum of the violet solution of **1** is typical for a distorted octahedral Co^{II} compound and it shows similar features as observed for other base adducts of bis(2,4-pentanedionato)cobalt(II).^[2,14] When a toluene solution of **1** is stored in a closed atmosphere it gradually transforms into a red colour over a number of days. The electronic spectrum of the red solution shows a broad absorption band with the maximum at 560 nm that is characteristic for an octahedral cobalt(III) species (Figure 1);^[14] however, traces of cobalt(II) might still be present. This transformation suggests the oxidation of Co^{II} to Co^{III} and indicates that the complex *cis*-[Co(acac)₂(Hdmpz)₂] is unstable in solution. Red crystals have been isolated, but these thin plates are prone to stacking faults. Although X-ray diffraction data were collected for one of the plates, the stacking disorder could not be resolved. However, a preliminary crystal structure solution revealed the presence of the cobalt ion surrounded by two 2,4-pentanedionato groups and two neutral Hdmpz ligands in the *trans* positions, showing that the assumed oxidation of Co^{II} to Co^{III} in **1** is accompanied by a *cis/trans* isomerisation process. Complex **2** does not display such solution redox behaviour.

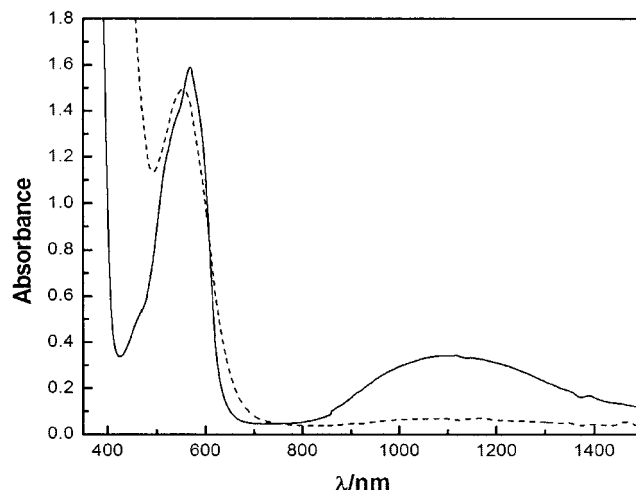


Figure 1. Spectral changes observed for a toluene solution of compound **1**; (a) just after preparation (—); (b) after 12 d (---)

Crystal Structures

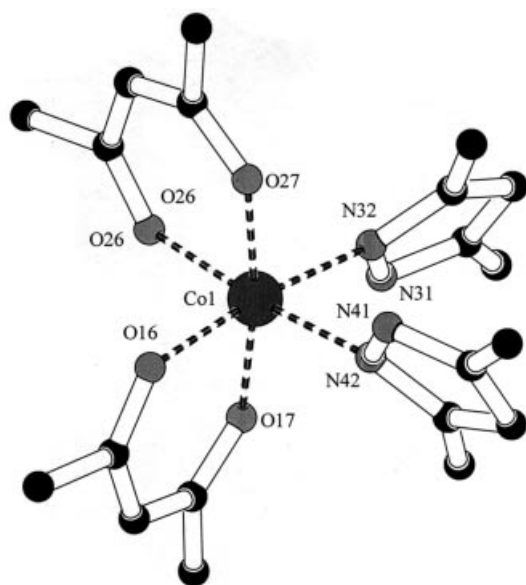
The structures of **1** and **2** were determined by X-ray crystallography. Selected bond lengths and angles are listed in Table 1.

As shown in Figure 2, the crystal structure of **1** consists of isolated *cis*-[Co(acac)₂(Hdmpz)₂] molecules. To the best of our knowledge, this is the first base adduct of bis(2,4-pentanedionato)cobalt(II) to contain the two monodentate ligands in *cis* positions. The cobalt ion is in a distorted octahedral environment; it is coordinated by four oxygen atoms from two chelating acetylacetonato groups and two nitrogen atoms from two monodentate Hdmpz ligands. The Co–O bond lengths, in the range 2.0571(17)–2.0978(18) Å, are similar to those reported for *trans*-[Co(acac)₂L₂] complexes. The Co–N bonds of 2.159(2) and 2.166(2) Å are shorter than the corresponding Co–N bonds in *trans*-[Co(acac)₂L₂] complexes with L = pyridine,^[5] 6-methylquinoline^[4] and 2-aminopyridine,^[6] but are longer than those observed for other Co^{II} complexes with 3,5-dimethylpyrazole.^[15,16] The most interesting feature of the crystal structure of **1** is the presence of hydrogen bonds that may play an important role in the stabilisation of the *cis* configuration of the monodentate ligands. The details of these interactions are presented in Table 2. The NH groups of both Hdmpz ligands each participate in one intramolecular and one intermolecular hydrogen bond. Thus, molecules of **1** are linked into one-dimensional chains along the *c*-direction by the propagation of two bifurcated hydrogen bonds of the N–H⋯(O)₂ type (Figure 3). The closest separation between the metal ions of neighbouring molecules is 6.1035(5) Å.

The molecular structure of [Co(acac)₂(Hdmea)] (**2**) is similar to that of **1** concerning the topology of the Co(acac)₂ moiety and the position of the donor atoms (Figure 4). The base adduct **2** is constrained to adopt the *cis* configuration due to the chelating nature of Hdmea. The Co^{II} ion has a distorted octahedral coordination sphere consisting of four oxygen atoms from two acetylacetonato

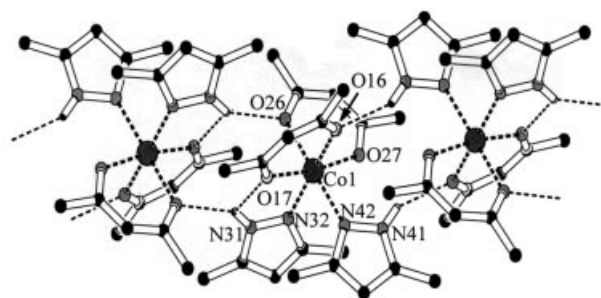
Table 1. Selected bond lengths [Å] and angles [°] for compounds **1** and **2**

<i>cis</i> -[Co(acac) ₂ (Hdmpz) ₂] (1)		[Co(acac) ₂ (Hdmea)] (2)	
Co1–O16	2.088(2)	Co1–O16	2.060(10)
Co1–O17	2.0571(17)	Co1–O17	2.036(7)
Co1–O26	2.0978(18)	Co1–O26	2.05(2)
Co1–O27	2.0604(17)	Co1–O27	2.070(8)
Co1–N32	2.159(2)	Co1–O31	2.15(2)
Co1–N42	2.166(2)	Co1–N34	2.237(7)
O16–Co1–O17	88.63(7)	O16–Co1–O17	89.2(4)
O16–Co1–O26	94.20(7)	O16–Co1–O26	97.9(7)
O16–Co1–O27	85.55(7)	O16–Co1–O27	89.6(5)
O16–Co1–N32	174.86(8)	O16–Co1–O31	89.8(8)
O16–Co1–N42	90.13(8)	O16–Co1–N34	167.84(12)
O17–Co1–O26	86.64(7)	O17–Co1–O26	92.7(8)
O17–Co1–O27	171.79(7)	O17–Co1–O27	178.61(7)
O17–Co1–N32	87.62(8)	O17–Co1–O31	91.5(8)
O17–Co1–N42	98.88(7)	O17–Co1–N34	87.9(3)
O26–Co1–O27	88.01(8)	O26–Co1–O27	88.0(8)
O26–Co1–N32	89.10(8)	O26–Co1–O31	171.24(13)
O26–Co1–N42	173.97(8)	O26–Co1–N34	94.0(7)
O27–Co1–N32	98.52(8)	O27–Co1–O31	88.0(8)
O27–Co1–N42	86.93(7)	O27–Co1–N34	93.2(3)
N32–Co1–N42	86.97(8)	O31–Co1–N34	78.5(7)

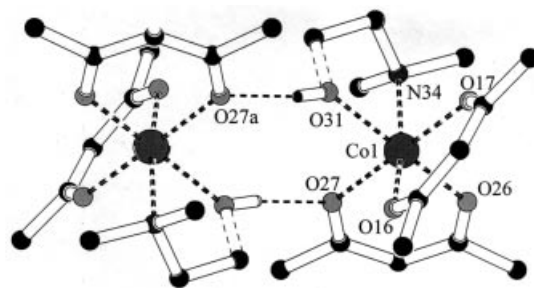
Figure 2. Pluton projection and atomic labels for *cis*-[Co(acac)₂(Hdmpz)₂] (**1**); hydrogen atoms are omitted for clarityTable 2. Hydrogen bond details (distances [Å] and angles [°]) for compounds **1** and **2**

Donor–H...Acceptor	D–H	H...A	D...A	D–H...A
<i>cis</i> -[Co(acac) ₂ (Hdmpz) ₂]:				
N(31)–H(31)...O(17)	0.88	2.63	3.030(3)	109
N(31)–H(31)...O(26) ^[a]	0.88	2.22	3.013(3)	151
N(41)–H(41)...O(27)	0.88	2.59	2.992(3)	109
N(41)–H(41)...O(16) ^[b]	0.88	2.28	3.067(3)	149
[Co(acac) ₂ (Hdmea)]:				
O(31)–H(31)...O(27) ^[c]	0.86(3)	1.87(5)	2.72(5)	170(30)

^[a] Symmetry transformations used to generate equivalent atoms: 2 – *x*, 1 – *y*, 1 – *z*. ^[b] 2 – *x*, 1 – *y*, –*z*. ^[c] –*x*, 1 – *y*, –*z*.

Figure 3. View of **1** showing the one-dimensional hydrogen-bonded chain

groups, as well as one oxygen and one nitrogen atom from a chelating Hdmea ligand. The Co–O bond lengths involving the 2,4-pentanedionato anions are in the range 2.036(7)–2.070(8) Å, slightly shorter than those in **1**; however, the Co1–O31 bond of 2.15(2) Å is longer. The Co1–N34 bond of 2.237(7) Å is significantly longer than the Co–N distances observed in **1**. In the crystal structure of **2**, the molecules are packed as dimers, as shown in Figure 4. Two strong O–H...O hydrogen bonds involving the

Figure 4. Atomic labels and view of the hydrogen-bonded dimer in **2**; only the major conformation of the disordered Hdmea ligand is shown

OH groups of the Hdmea molecules and 2,4-pentanedionato O atoms link each pair of molecules (Table 2). The separation between the metal ions of neighbouring molecules is 5.47(9) Å.

EPR Spectroscopy and Magnetic Properties

The EPR spectra of polycrystalline *cis*-[Co(acac)₂(Hdmpz)] and [Co(acac)₂(Hdmea)] recorded at 4.2 K are shown in Figure 5. As previously observed for *trans* adducts of bis(2,4-pentanedionato)cobalt(II),^[17] the large anisotropy of cobalt(II) complexes is such that the intermolecular exchange interactions do not cause exchange narrowing and the signals of individual molecules are resolved. However, the high- and low-field features are very broad, due to unresolved metal hyperfine coupling. Assuming an effective $S = 1/2$ ground state and neglecting interactions between the two Co^{II} ions, the following g -values are obtained;^[18] for **1** they are: $g_1 = 2.1$, $g_2 = 2.5$ and $g_3 = 6.5$; for **2** they are: $g_1 = 1.9$, $g_2 = 4.3$ and $g_3 = 10.7$. The large variation of the g -values is expected in view of the high sensitivity of the g -values of Co^{II} with respect to any weak distortion of the ligand field. The average g -value ($\langle g \rangle$) of complex **1** ($\langle g \rangle = 3.7$) is similar to those observed for distorted octahedral cobalt(II) complexes. For such complexes, $\langle g \rangle = 4.3$ and g -tensor components in the range from 1.5 to 7 have been reported.^[19] For compound **2**, $\langle g \rangle = 5.6$ and g_3 are larger than usual.

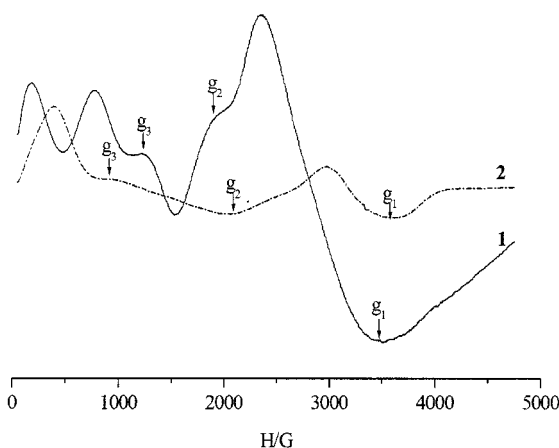


Figure 5. EPR spectra of polycrystalline powders of **1** and **2** recorded at 4.2 K and 9 GHz

The magnetic properties of **1** and **2** were investigated in the range 5–300 K. The $\chi_m T$ product at room temperature is 1.92 emu·K·mol⁻¹ for **1** and 2.19 emu·K·mol⁻¹ for **2**. Both values are slightly larger than the spin-only value for an isolated high-spin Co^{II} centre (1.875 emu·K·mol⁻¹ for $S = 3/2$ assuming $g_{Co} = 2$) because of the orbital contribution. The $\chi_m T$ curves of both compounds exhibit a continuous decrease as the temperature is lowered from 300 to 5 K. Such behaviour, characteristic for Co^{II} complexes, is essentially due to single-ion anisotropy which may be com-

bined with minor contributions from antiferromagnetic exchange between the Co^{II} centres by hydrogen bonds.

Electron Structure Analysis of the Ligand Binding in Complexes **1** and **2**

A synoptic perception of the coordination bonding is obtained using the Laplacian of electron density and the density difference maps drawn in the ligand planes. The following results are based on the unrestricted DFT-B3LYP calculation with the 6-31G basis set.^[20,21] The Laplacian pattern of each coordinated ligand [Figure 6 (a–c)] is in its gross part similar to those of the free ligands. The metal ion is mapped in complexes by areas with $\nabla^2\rho > 0$, corresponding to the electron-density depletion due to its ionic positive status.^[22,23] The Laplacian can in principle detect the location of the lone pairs among the areas with $\nabla^2\rho > 0$. Figure 6 (a–c) shows, however, that the lone pairs are not very prominent at the oxygen donors, but are more pronounced at the nitrogen donor atoms. A similar aspect is observed comparing the different donor atoms of the amino alcohol ligand Hdmea. This may be due to the high chemical hardness of the oxygen atoms as compared to nitrogen atoms (the resistance of the electron cloud to deformations).

The formation of lone pairs in the valence shell is revealed in a rather spectacular way by taking the difference of the electron density of the ligand in the complex and that of the free ligand (taken in the same location and with the same geometry). In these representations [Figure 6 (d–f)] the lone pairs are detected as density depletion areas (dashed, grey contours). This is practically a direct visualisation of the density flow corresponding to the donation of the lone pair towards the metal ion.

Another method suitable for the detection and the analysis of lone pairs is the Natural Bond Orbital theory.^[24,25] The orbital pictures in Figure 7 were drawn with the “molekel” PC program.^[26] Surprisingly, for the 2,4-pentanedionato ligand it was found that the coordinating lone pairs have a content of about $s(10\%)p(90\%)$ [see $\lambda_1(O)$ and $\lambda_1(O')$ in Figure 7], rather than the $s(33\%)p(67\%)$ character of the expected sp^2 hybrids. Besides, the λ_1 hybrids are not perfectly aligned along the Co–O axis, which has a deviation of about 10° inward of the chelating ring. The noncoordinating lone pairs at the oxygen atoms (denoted λ_2 in Figure 7) have approximately an $s(50\%)p(50\%)$ composition and are inclined toward the metal ion with an angle of about 100° (instead of the expected 120°). The higher content in p character at the coordinating lone pairs $\lambda_1(O)$ may be interpreted as favourable to the coordination process, because the lower ionisation potential of the p shell as compared to s ensures a better σ -donor action. This effect occurs at the expense of a lower p content at λ_2 . The hybrid of the oxygen atom devoted to the $\sigma(C-O)$ bond has approximately $s(40\%)p(60\%)$ composition, which is closer to the expected sp^2 scheme. The composition of the hybrids around the oxygen atom in the M–O–C plane practically sums up to the total sp^2 content. Surprisingly, the above-mentioned nonstandard compositions of lone pairs represent a real electronic structure effect that remains quali-

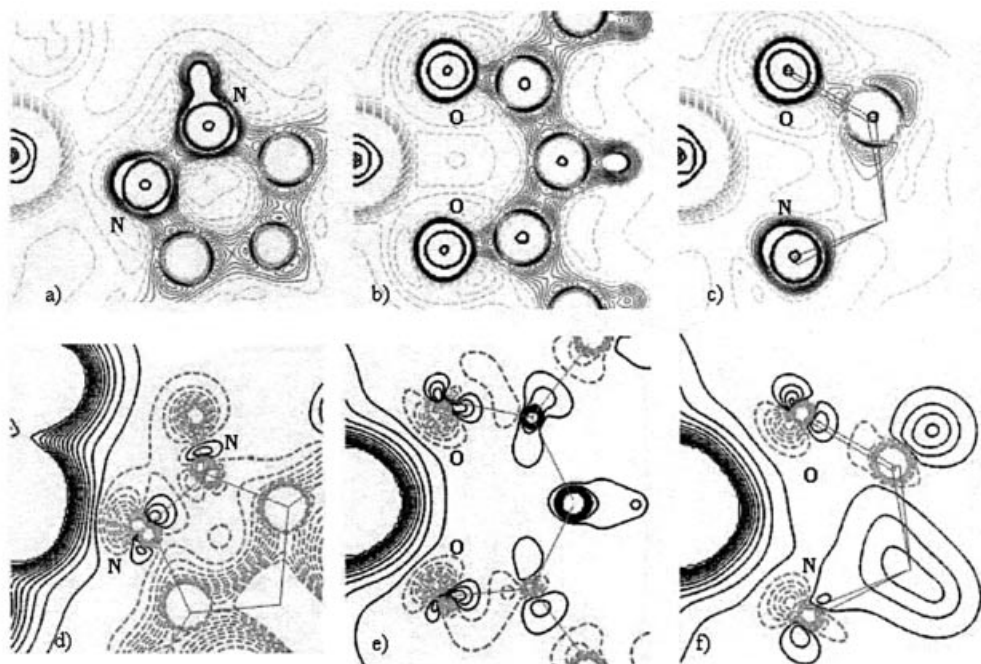


Figure 6. The electron-density descriptors applied to the ligands in complexes **1** and **2**: (a), (b) and (c) the Laplacian density maps in the CoNN, CoOO and CoON coordination planes of pyrazole, acac and amino alcohol Hdmea, respectively; in (d), (e) and (f) the electron density difference maps (complex minus free ligand) are presented for the same series of ligands; the acac ligand shown is taken from complex **1**, the situation for complex **2** being quite similar; in all the figures the dark, continuous lines correspond to density accumulation, dashed lines to depletion areas

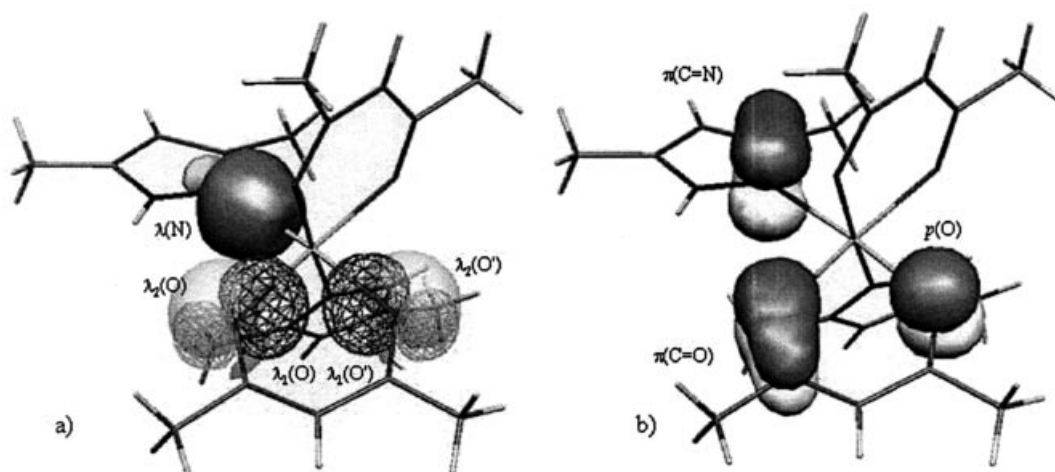


Figure 7. a) The σ -type lone pairs and b) p - π coordinating bond orbitals of the 2,4-pentanedionato and pyrazole ligands resulting from the application of NBO analysis on **1**

tatively stable at different levels of calculation. The calculated situation does not offend the concept of sp^2 hybridisation.

Keeping in mind that the sp^2 concept is only a qualitative or average rule, a careful look at the data offered by NBO analysis provides interesting new information for chemical intuition. It should be noted that the regular sp^2 hybridisation at a symmetric AX_3 triangular substitution of a main group central atom means that the three necessary orbitals are decided by symmetry to be one s plus two p (in plane) orbitals. The sp^2 notation is a convention concerning, in

fact, the sum of hybrid compositions. Each of the equivalent hybrids can be more precisely noted $s^{1/3}p^{2/3}$, namely with $s(33.33\%)p(66.67\%)$ composition. When the substituents at the central atom are of a different chemical nature, the electronegativity difference is a supplementary factor that determines the s/p content of each hybrid (keeping the total sp^2 composition). In the same respect, when the angles between substituents differ from the ideal 120° , the detailed composition should vary due to trigonometric reasons in order to accomplish the orientation of the hybrids along the bond. In certain circumstances the electronegativity versus

geometric factors may result in slight deviations of the hybrid orbitals from the bond axis, as is the case in the coordinating lone pair.

Conclusion

The synthesis and characterisation of two new base adducts of bis(2,4-pentanedionato)cobalt(II) with 3,5-dimethylpyrazole (Hdmpz) and dimethylethanolamine (Hdmea) are reported. The crystal structures of **1** and **2** show mononuclear Co^{II} complexes with *cis*-distorted octahedral geometries; these complexes are linked by hydrogen bonds between the coordinated 2,4-pentanedionato anions and the neutral Hdmpz or Hdmea ligands. In solution, compound **1** is kinetically unstable. Its slow oxidation into a Co^{III} complex is accompanied by a *cis/trans* isomerization. In contrast, complex **2** does not display this behaviour. In subsequent studies the results presented here will be applied to the investigation of the antioxidant properties of these complexes as antiskinning agents in alkyd paints. The properties of chelating ligands, constrained to adopt *cis* geometry, may be compared with those of monodentate ligands, which typically yield *trans* complexes except in the case of the Hdmpz complex reported here. Interesting particularities of the lone pair topology at the pentanedionato ligands were revealed with the help of various analyses based on DFT calculations.

Experimental Section

General Remarks: All chemicals were of reagent grade, and were used as received. The anhydrous cobalt acetylacetonate was syn-

thesised as previously reported.^[27] All experiments were carried out in air. Elemental analyses for C, H and N were performed with a Perkin–Elmer 2400 Series II analyzer. Infrared spectra (4000–300 cm^{−1}) were recorded with a Perkin–Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. UV/Vis spectra were obtained with a Perkin–Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique, with MgO as the reference. X-band EPR spectra were recorded with a Bruker Elexsys 680 spectrometer using a rectangular cavity with an Oxford flow cryostat. Magnetic susceptibility measurements (5–300 K) were carried out at 1000 G using a Quantum Design MPMS-5 5T SQUID magnetometer. Data were corrected for magnetisation of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants.

[Bis(acetylacetonato)bis(3,5-dimethylpyrazole)Co^{II}] (1): Compound **1** was synthesised by adding 3,5-dimethylpyrazole (0.384 g, 4 mmol) to a hot solution of anhydrous cobalt acetylacetonate (0.513 g, 2 mmol) in toluene (20 mL) and stirring for 1 h. The resulting solution was allowed to stand at room temperature; violet crystals of **1** formed overnight. These were collected by filtration, washed with methanol and dried in air. Yield 0.75 g (83%). C₂₀H₃₀CoN₄O₄ (449.81): calcd. C 53.40, H 6.66, N 12.44; found C 53.63, H 6.32, N 12.66. IR: $\tilde{\nu}$ = 3284 (N–H), 2923 (C–H), 1595 (C=N), 1571 (C–O), 1516 (C–C), 1357 (C–H), 1014 (C–H), 765 (C–H) cm^{−1}. UV/Vis/NIR: $\tilde{\nu}_{\text{max}}$ = 8547, 19607 cm^{−1}.

[Bis(acetylacetonato)(dimethylethanolamine)Co^{II}] (2): Compound **2** was synthesised by adding *N,N*-dimethylethanolamine (0.178 g, 2 mmol) to a hot solution of anhydrous cobalt acetylacetonate (0.513 g, 2 mmol) in toluene (20 mL) and stirring for 1 h. The resulting solution was allowed to stand at room temperature for 5 d during which time red crystals formed. These were collected by filtration, washed with diethyl ether and dried in air. Yield 0.92 g (67%). C₁₄H₂₅CoNO₅ (346.02): calcd. C 48.59, H 7.22, N 4.04; found C 48.03, H 6.90, N 4.23. IR: $\tilde{\nu}$ = 3348 (O–H), 2918 (C–H),

Table 3. Crystallographic data for compounds **1** and **2**

	<i>cis</i> -[Co(acac) ₂ (Hdmpz) ₂] (1)	[Co(acac) ₂ (Hdmea)] (2)
Empirical formula	C ₂₀ H ₃₀ CoN ₄ O ₄	C ₁₄ H ₂₅ CoNO ₅
Formula mass	449.41	346.28
Crystal system	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> [Å]	9.8218(2)	7.824(11)
<i>b</i> [Å]	10.3638(2)	10.36(2)
<i>c</i> [Å]	12.1242(3)	12.0(2)
α [°]	97.558(1)	105.4(4)
β [°]	98.579(1)	104.5(3)
γ [°]	117.369(1)	98.21(18)
<i>V</i> [Å ³]	1055.22(4)	885(15)
<i>Z</i>	2	2
<i>D</i> _{calcd.} [g cm ^{−3}]	1.41	1.30
μ (Mo–K α) [mm ^{−1}]	0.847	0.988
Crystal size [mm]	0.450 × 0.045 × 0.045	0.40 × 0.40 × 0.08
<i>T</i> [K]	150	293
Data collected	17051	8245
Unique data	4829	4064
<i>R</i> _{int}	0.086	0.033
<i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>)]	0.050	0.035
<i>R</i> _w (<i>F</i> ²)	0.100	0.110
<i>S</i>	0.96	1.08
$\Delta\rho_{\text{min}}, \Delta\rho_{\text{max}}$ [e·Å ^{−3}]	−0.43, 0.43	−0.37, 0.33

2820 (C–H), 1654 (C–N), 1575 (C–O), 1557 (C–C), 1386 (C–H), 1015 (C–H), 751 (C–H) cm^{-1} . UV/Vis/NIR: $\tilde{\nu}_{\text{max}} = 8889$, 19920 cm^{-1} .

X-ray Crystal Structure Analysis: Intensity data for a single crystal were collected using Mo- K_{α} radiation ($\lambda = 0.71073 \text{ \AA}$) with either a Nonius Kappa CCD diffractometer with a rotating anode as for **1**, or with an Enraf–Nonius CAD4 diffractometer with a sealed tube for **2**. A correction for absorption was considered unnecessary in both cases. The structures were solved by automated Patterson methods using DIRDIF99,^[28] and were refined on F^2 by least-squares procedures using SHELXL-97.^[29] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydroxy hydrogen atom in **2** was refined freely with an isotropic displacement parameter. All other hydrogen atoms were constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. In **2**, the Hdmea ligand is disordered over two conformations, with refined relative occupancies of 0.845(5):0.155. Structure validation and molecular graphics preparation were performed with the PLATON package.^[30] Crystallographic data are presented in Table 3. CCDC-219606 (for **1**) and -219607 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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